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Structures and Energies of 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[1]

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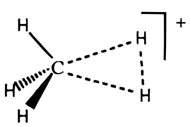
Structures and energies of the parent hexa-, hepta-, and octacoordinate alonium ions AlH_6^+, AlH_7^{2+}, and AlH_8^{3+}, respectively, were calculated at the ab initio MP2/6-31G** and QCISD(T)/6-311G** levels. The C_{2v} symmetrical **4**, C_{3v} symmetrical **7**, and T_d symmetrical **10** were found to be the energy-minimum structures of AlH_6^+, AlH_7^{2+}, and AlH_8^{3+}, respectively. The related structures of AlH_4^+ (**6**), AlH_5^{2+} (**9**), and AlH_6^{3+} (**11**) were also calculated at the ab initio MP2/6-31G** level. Formation of AlH_6^+ by protonation of AlH_5 was found to be strongly exothermic by 181.0 kcal/mol. The protonation of AlH_3 to AlH_4^+ (**6**) is also highly exothermic by 176.4 kcal/mol.

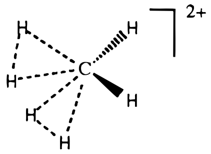
Introduction

Higher coordinate[2] main group compounds are of substantial theoretical[3] and experimental[4] interest. Schmidbaur et al. have prepared a variety of monopositively charged higher coordinate gold complexes of main group elements.[4] They have also prepared dipositively charged carbon[5] $\{[(C_6H_5)_3PAu]_6C\}^{2+}$, nitrogen[6] $\{[(C_6H_5)_3PAu]_5N\}^{2+}$, phosphorus[7] $\{[(C_6H_5)_3PAu]_5P\}^{2+}$, sulfur[8] $\{[(C_6H_5)_3PAu]_4S\}^{2+}$, and oxygen[9] $\{[(o\text{-}CH_3C_6H_4)_3PAu]_4O\}^{2+}$ complexes and determined their X-ray structures. These represent isolobal analogues of CH_6^{2+}, NH_5^{2+}, PH_5^{2+}, SH_4^{2+}, and OH_4^{2+}, respectively.

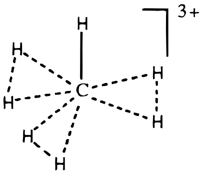
Calculated parent five-, six-, and seven-coordinate carbocations CH_5^+ (**1**),[10] CH_6^{2+} (**2**),[11] and CH_7^{3+} (**3**),[12] respectively, have one, two, and three 2e-3c bonding interactions in their minimum-energy structures. 2e-3c interactions in hypercoordinate carbocations are very significant, although their natures vary from one molecule to another.



1 CH_5^+ C_s



2 CH_6^{2+} C_{2v}



3 CH_7^{3+} C_{3v}

We recently reported[13] the calculated structures and energies of the parent hexa-, hepta-, and octacoordiate boronium ions BH_6^+, BH_7^{2+}, and BH_8^{3+}. The structures of BH_6^+ and BH_7^{2+} were found to be isostructural with their isoelectronic carbon analogues CH_6^{2+} (**2**) and CH_7^{3+} (**3**), respectively. Eight hydrogen atoms of BH_8^{3+} structure are found to be bonded to the boron atom by four 2e-3c bonds. In continuation of our study of hypercoordinate compounds, we have now extended our investigations to the parent hexa-, hepta-, and octacoordiate alonium ions AlH_6^+, AlH_7^{2+}, and AlH_8^{3+}, respectively, by ab initio calculations. Recently, Schreiner et al.[14] calculated the structures and energies of AlH_5. The authors concluded that AlH_5 can exist as a weak complex between AlH_3 and dihydrogen

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Table 1. Calculated Total Energies, −au (ZPE,[a] kcal/mol)

	MP2/6-31G**// MP2/6-31G**	G2	QCISD(T)/6-311G**// QCISD(T)/6-311G**
AlH_6^+ (**4**)	245.14777 (25.8)	245.20925	245.21216
AlH_6^+ (**5**) TS	245.08807 (26.0)	245.15330	
AlH_4^+ (**6**)	243.98065 (16.3)	244.03507	
AlH_7^{2+} (**7**)	245.18522 (30.3)	245.24276	245.25416
AlH_7^{2+} (**8**) TS	245.10841 (30.1)	245.16940	
AlH_5^{2+} (**9**)	243.99496 (20.3)	244.04601	
AlH_8^{3+} (**10**)	244.99517 (32.8)	245.05235	245.06758
AlH_6^{3+} (**11**)	243.77040 (23.4)	243.81934	
AlH_3	243.69034 (11.2)	243.75396	
AlH_5	244.84928 (19.0)	244.92086	
AlH_2^+	242.81420 (6.5)	242.86067	
H_3^+	1.32428 (12.6)	1.32445	

[a] Zero-point vibrational energies (ZPE) at MP2/6-31G**//MP2/6-31G** scaled by a factor of 0.93.

Table 2. MP2/6-31G** (QCISD(T)/6-311G**) Calculated Lowdin Bond Orders and Charges[a]

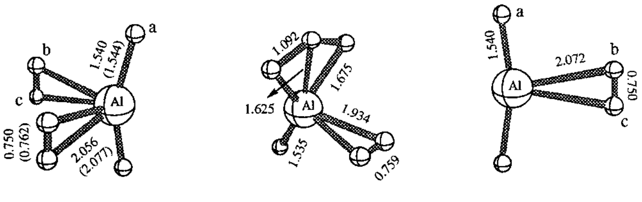
no.	bond	bond order	atom	charge
4	$Al-H_a$	0.98 (0.97)	Al	+1.44 (+1.41)
	$Al-H_b$	0.21 (0.20)	H_a	−0.32 (−0.32)
	H_b-H_c	0.77 (0.79)	H_b	+0.05 (+0.06)
6	$Al-H_a$	0.98	Al	+1.59
	$Al-H_b$	0.21	H_a	−0.34
	H_b-H_c	0.78	H_b	+0.04
7	$Al-H_a$	0.96 (0.97)	Al	+1.60 (+1.58)
	$Al-H_b$	0.29 (0.27)	H_a	−0.18 (−0.19)
	$Al-H_c$	0.31 (0.28)	H_b	+0.15 (+0.15)
	H_b-H_c	0.66 (0.70)	H_c	+0.04 (+0.06)
9	$Al-H_a$	0.95	Al	+1.81
	$Al-H_b$	0.30	H_a	−0.16
	$Al-H_c$	0.32	H_b	+0.14
	H_b-H_c	0.65	H_c	+0.04
10	$Al-H_a$	0.36 (0.33)	Al	+1.84 (+1.81)
	$Al-H_b$	0.36 (0.33)	H_a	+0.14 (+0.15)
	H_a-H_b	0.58 (0.62)	H_b	+0.15 (+0.15)
11	Al−H	0.39	Al	+2.14
	H_a-H_b	0.54	H	+0.14

[a] For numbering scheme, see Figures 1−3.

at low temperature. Olah et al. also studied[15] the protonation of AlH_4^- previously and obtained evidence via H−D exchange for the intermediacy of AlH_5 (or its isotopomers). However, calculations show that intramolecular hydrogen scrambling in AlH_5 prior to dissociation into AlH_3 and H_2 is unlikely,[14] and thus observed exchange could have been the consequence of the reaction of formed HD with alane or protonation (deuteration) of AlH_5 to AlH_6^+ (or that of the corresponding isotopomers).

Calculations

Calculations were carried out with the Gaussian 94 program system.[16] Geometry optimizations and frequency calculations were performed at the MP2/6-31G** and QCISD(T)/6-311G** levels. From calculated frequencies, the optimized structures were characterized as minima (NIMAG = 0) or transition structures (NIMAG = 1). Furthermore, the transition structures were examined by IRC calculations.[18] For improved energy, the Gaussian-2 (G2) energies[17] were computed. MP2/6-31G** geometrical parameters and G2 calculated energies will be discussed throughout, unless stated otherwise. Calculated energies are given in Table 1. Atomic charges and Lowdin[19] bond orders were obtained using the natural bond orbital analysis (NBO)[20] method (Table 2). Calculated vibrational frequencies are given in Table 3.



4 C_{2v} **5** C_s **6** C_{2v}

Figure 1. MP2/6-31G** (QCISD(T)/6-311G**) structures of **4**−**6**.

Scheme 1

		ΔH (kcal/mol)[a]
$AlH_5 + H^+$ -------> AlH_6^+ (**4**)	(1)	-181.0
$AlH_3 + H_3^+$ -------> AlH_6^+ (**4**)	(2)	-82.1
$AlH_3 + H^+$ -------> AlH_4^+ (**6**)	(3)	-176.4
AlH_4^+ (**6**) + H_2 -------> AlH_6^+ (**4**)	(4)	-4.9
AlH_6^+ (**4**) + H^+ -------> AlH_7^{2+} (**7**)	(5)	-21.0
AlH_4^+ (**6**) + H_3^+ -------> AlH_7^{2+} (**7**)	(6)	+73.3
AlH_4^+ (**6**) + H^+ -------> AlH_5^{2+} (**9**)	(7)	-6.9
AlH_5^{2+} (**9**) + H_2 -------> AlH_7^{2+} (**7**)	(8)	-19.1
AlH_7^{2+} (**7**) + H^+ -------> AlH_8^{3+} (**10**)	(9)	+119.5
AlH_5^{2+} (**9**) + H_3^+ -------> AlH_8^{3+} (**10**)	(10)	+199.6
AlH_5^{2+} (**9**) + H^+ -------> AlH_6^{3+} (**11**)	(11)	+142.2
AlH_6^{3+} (**11**) + H_2 -------> AlH_8^{3+} (**10**)	(12)	-41.8
$AlH_2^+ + H_2$ -------> AlH_4^+ (**6**)	(13)	-5.1

[a] *with the G2 method*

Results and Discussion

AlH_6^+. C_{2v} symmetrical structure **4** was found to be the only minimum on the potential energy surface of AlH_6^+ (Figure 1). Structure **4** has two 2e-3c bonds and two 2c-2e bonds and can be considered as a complex between AlH_2^+ and two hydrogen molecules. Structure **4** is isostructural with hexacoordinate boron[13] BH_6^+ as well as carbon[11] CH_6^{2+}. At the MP2/6-31G** level, the Al−H bond distance the of 2e-3c bond is 2.056 Å, significantly longer than that of the 2c-2e bond (1.540 Å). The H−H 2e-3c bond length is 0.762 Å, only 0.028 Å longer than that of H_2 molecule at the same level. These results indicate that the interaction between H_2 and the aluminum atom in the 2e-3c bond of **4** is weak. This is in agreement with the calculated Lowdin[19] bond orders of Al−H and H−H bonds (Table 2). Thus the Al−H bond order of the 2e-3c bond is only 0.21, less than a quarter of that of the 2c-2e bond (0.98). On the other hand, the H−H bond order of the 2e-3c bond is 0.77, only 0.23 less than that of neutral H_2.

We found that the protonation of AlH_5 to form C_{2v} AlH_6^+ (**4**) is highly exothermic by 181.0 kcal/mol (eq 1, Scheme 1), which is even 17.9 kcal/mol more exothermic than that of

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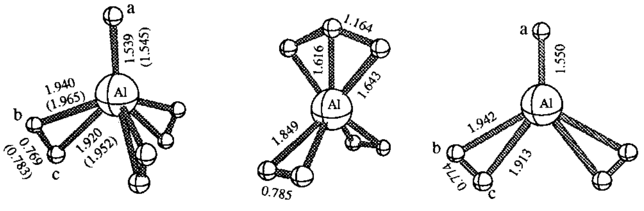
Table 3. MP2/6-31G** Calculated Frequencies[a] and IR Intensities

no.	frequencies, cm^{-1} (intensities, KM/mol)
4	303 (0), 339 (0), 911 (0), 346 (0), 493 (0), 498 (7), 558 (268), 562 (245), 690 (43), 704 (75), 924 (0), 930 (50), 2132 (5), 2205 (28), 4349 (93), 4353 (91)
6	364 (0), 499 (4), 541 (271), 592 (185), 697 (51), 901 (28), 2127 (2), 2209 (16), 4349 (110)
7	210 (0), 218 (4), 352 (0), 380 (1), 438 (164), 907 (114), 928 (21), 987 (174), 995 (21), 2143 (48), 4088 (788), 4113 (89)
9	122 (0), 126 (4), 330 (32), 377 (1), 381 (65), 899 (99), 904 (85), 1009 (8), 1011 (72), 2074 (127), 4021 (539), 4047 (226)
10	114 (0), 320 (3), 326 (15), 328 (1), 330 (5), 822 (4), 827 (182), 829 (203), 836 (175), 1117 (0), 1157 (0), 3715 (2016), 3801 (0)
11	82 (0), 92 (0), 213 (28), 293 (13), 781 (88), 795 (417), 1149 (0), 1210 (3), 3500 (1902), 3600 (0)

[a] Not scaled.



7 C_{3v} **8** C_{2v} **9** C_{2v}

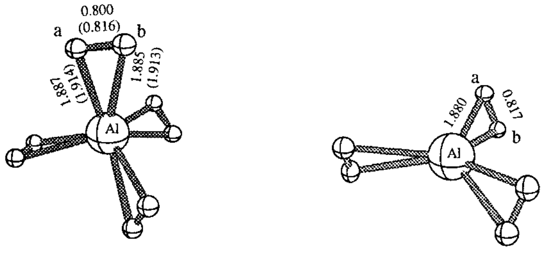
Figure 2. MP2/6-31G** (QCISD(T)/6-311G**) structures of **7**−**9**.

protonation of water. However, the transition state for the deprotonation process could not be located. Structure **5** (Figure 1), which lies 35.1 kcal/mol higher in energy than structure **4**, was located as transition structure for hydrogen scrambling in **4**. Thus, hydrogen scrambling in cation **4** through transition state **5** has a considerable kinetic barrier. The dissociation of **4** into AlH_3 and H_3^+ (eq 3) is calculated to be endothermic by 82.1 kcal/mol (Scheme 1).

Olah et al. previously investigated[15] the protonation of AlH_4^- in strong acids such as H_2SO_4 and HF and suggested evidence by H−D exchange for the intermediacy of AlH_5. However, hydrogen scrambling in AlH_5 prior to dissociation into AlH_3 and H_2 was calculated to be an unfavorable process.[14] Hydrogen scrambling in AlH_5 was calculated to have a high 26.0 kcal/mol kinetic barrier. It is thus probable that indeed AlH_6^+ is formed in the acidic solutions and is responsible for the observed scrambling.

Structure **4** can also be viewed as a complex between AlH_4^+ and H_2. Structure **6**, a planar C_{2v} form with a 2e-3c interaction, was found be the global minimum for AlH_4^+ (Figure 1). Similar structures were also calculated for carbon[21] (CH_4^{2+}) and boron[13] (BH_4^+) analogues. Protonation of AlH_3 to give **6** was also found to be highly exothermic by 176.4 kcal/mol. On the other hand, the reaction $AlH_4^+ + H_2$ (eq 4) is only 4.9 kcal/mol exothermic. In comparison, the reaction $AlH_3 + H_2$ is endothermic by 3.1 kcal/mol.[14]

AlH_7^{2+}. The C_{3v} structure **7** is the only minimum that was located on the potential energy surface of AlH_7^{2+}. Structure **7** is characterized by three 2e-3c bonds and a 2c-2e bond and resembles a complex between AlH^{2+} and three hydrogen molecules (Figure 2). Structure **7** is isostructural with that of CH_7^{3+}[12] and BH_7^{2+}.[13] The Al−H bond distances of 2e-3c interactions are 1.940 and 1.920 Å, slightly shorter than that of **4**. This indicates that the 2e-3c interaction between H_2 and Al is probably stronger in **7** than in **4**. The calculated 2e-3c Al−H bond order of **7** is therefore slightly larger than that of **4** (Table 2). We have also calculated the transition structure **8** for intramolecular hydrogen transfer in the trication (Figure 2). Structure **8** lies 46.0 kcal/mol higher in energy than structure **7**. Hydrogen scrambling in **7** therefore also has high kinetic barrier. On the other hand, hydrogen scrambling was calculated to be facile for BH_7^{3+}[1] and CH_7^{3+}.[12] The dissociation of **7** into **4** and H^+ (eq 4) is 21.0 kcal/mol endothermic, whereas that into AlH_4^+ and H_3^+ (eq 6) is exothermic by 73.3 kcal/mol (Scheme 1).



10 (T_d) **11** D_3

Figure 3. MP2/6-31G** (QCISD(T)/6-311G**) structures of **9** and **10**.

Ion **7** can also be considered as a complex between AlH_5^{2+} and H_2. The structure of **9** is of a planar C_{2v} symmetry with two 2e-3c bonds and a 2c-2e bond. A similar structure has also been reported[22] for BH_5^{2+}. Formation of **9** by protonation of AlH_4^+ (**6**) is exothermic by 6.9 kcal/mol (eq 7). Formation of **7** from the reaction of **9** with H_2 is also exothermic by 19.1 kcal/mol (eq 8).

AlH_8^{3+}. We have also calculated the minimum-energy structure **10** for the octacoordinate trication AlH_8^{3+}. The structure resembles a complex of four H_2 molecules bound to a tripositively charged aluminum atom, Al^{3+} (Figure 3). A similar structure was also calculated for the octacoordinate boronium trication BH_8^{3+}.[13] In contrast, the parent octacoordinate carbonium tetracation CH_8^{4+} was not found to be a stable species at the MP2/6-31G** level probably due to excessive charge−charge repulsion.[12] In comparison with those of **4** and **7**, the H_2 units of the 2e-3c interactions of **10** are more tightly bound to the aluminum atom. Thus, the Al−H bond distances of the 2e-3c interactions (1.887 and 1.885 Å) are shorter than those of **4** and **7**. The calculated Al−H bond orders are also considerably higher than those of **4** and **7**. The dissociation of the trication into **7** and H^+ (eq 9) and into AlH_5^{2+} and H_3^+ (eq 10) are calculated to be exothermic by 119.5 and 199.6 kcal/mol, respectively (Scheme 1). From eqs 6, 9, and 13 it can be seen that, whereas the formation of AlH_4^+ (**6**) from AlH_2^+ and H_2 is slightly favorable thermodynamically, the formation of AlH_7^{2+} (**7**) and subsequently AlH_8^{3+} (**10**) is strongly unfavorable.

The related hexacoordinate trication AlH_6^{3+} (**11**), which can complex with H_2 to form **10**, was also calculated. The minimum structure of AlH_6^{3+} is a propeller-shaped molecule with three 2e-3c bonds. The plane of each 2e-3c unit is rotated 65.5° around its axis from the plane of the molecule at the MP2/6-31G** level. The calculated[22] structure of BH_6^{3+} is also a propeller-shaped molecule with three 2e-3c bonds. But the

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plane of each of the 2e-3c unit in BH_6^{3+} is rotated only 1.6° around its axis from the plane of the molecule at the same MP2/6-31G** level. Formation of **11** by protonation of AlH_5^{2+} (**9**) is highly endothermic by 142.2 kcal/mol (eq 11). On the other hand, reaction of **11** and H_2 is exothermic by 41.8 kcal/mol (eq 12).

We also calculated the NBO charges[20] of the alonium ions (Table 2). The charges of the aluminum atom in the ions **4**, **7**, and **10** are 1.44, 1.60, and 1.84 au, respectively. This indicates that the aluminum atoms bear the most of the positive charge. In contrast, the hydrogen atoms of the corresponding analogous boron cations bear most of the positive charge.[13] This is consistent with the better hydride donor ability of aluminum compounds compared to that of the boron analogues.[14]

Our present studies show that the hexa- and heptacoordinate alonium ions AlH_6^+ (**4**) and AlH_7^{2+} (**7**), with two and three 2e-3c bonds, respectively, are isostructural with their boron analogues BH_6^+ and BH_7^{2+} as well as carbon analogues CH_6^{2+} (**2**) and CH_7^{3+} (**3**). The octacoordinate alonium ion AlH_8^{3+} (**10**), with four 2e-3c bonds, is isostructural with the boron analogue BH_8^{3+}. Calculated charges and protonation energies are consistent with the better hydride donor ability of aluminum compounds compared to that of boron analogues.[13] The instability of the trication AlH_8^{3+} (**10**) is mainly due to the charge−charge repulsion, and if formed, it will probably dissociate spontaneously into AlH_7^{2+} (**7**) and H^+. An implication of the study of these ions is the relationship of their bonding nature (2e-3c bonds) to that of Schmidbaur type gold complexes,[4] although, in the latter complexes, substantial metal−metal bonding (which exceeds 2e-3c) makes them stable and even isolable as crystalline salts.

Conclusions

Structures and energies of the parent hexa-, hepta-, and octacoordinate alonium ions AlH_6^+ (**4**), AlH_7^{2+} (**7**), and AlH_8^{3+} (**10**), respectively, were calculated at the ab initio MP2/6-31G** and QCISD(T)/6-311G** levels of theory. The cations, with eight valence electrons, C_{2v} symmetrical **4**, C_{3v} symmetrical **7**, and T_d symmetrical **10**, are isostructural with their boron analogues[13] BH_6^+, BH_7^{2+}, and BH_8^{3+}, respectively, and are stabilized by two, three, and four 2e-3c bonds. The local geometry around the aluminum atom is therefore expectedly roughly tetrahedral, the substituent being a hydrogen atom or a dihydrogen molecule. The structures of related AlH_4^+ (**6**), AlH_5^{2+} (**9**), and AlH_6^{3+} (**11**), with six valence electrons, were also calculated at the ab initio MP2/6-31G** level. The local geometry around the aluminum atom is therefore expectedly roughly planar trigonal, the substituent being a hydrogen atom or a dihydrogen molecule. The protonation of AlH_5 to form AlH_6^+ (**4**) is calculated to be highly exothermic by 181.0 kcal/mol and may be responsible for the experimentally observed hydrogen−deuterium scrambling of AlH_4^- in superacid solutions. The protonation of AlH_3 to form AlH_4^+ (**6**) is very exothermic by 176.4 kcal/mol.

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