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Structure, Spectra, and Reaction Energies of the Aluminum−Nitrogen $(HAl-NH)_2$ and $(H_2Al-NH_2)_2$ Rings and the $(HAl-NH)_4$ Cluster

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Rings of four-coordinate aluminum and nitrogen are easily synthesized and well studied, as are clusters of four-coordinate Al and N. Only recently, however, have rings that are derivatives of the model compounds $(HAl-NH)_n$ ($n = 2, 3$) with three-coordinate Al and N been synthesized. Ab initio investigations of the structure, bonding, vibrational spectra, and reaction energies for the three-coordinate ring $(HAl-NH)_2$, the four-coordinate ring $(H_2Al-NH_2)_2$, and the four-coordinate cluster $(HAl-NH)_4$ are presented. Even in the absence of differences in steric factors, the four-membered ring has longer Al−N bonds than either the six-membered ring or the unassociated aluminum amide, H_2Al-NH_2. This is due to both rehybridization and π interactions. Theoretical reaction energies for formation of the $(HAl-NH)_4$ cluster from the $(H_2Al-NH_2)_2$ ring are consistent with intermolecular loss of hydrogen, or the necessity of surface catalysis.

Introduction

Aluminum−nitrogen rings and clusters hold both theoretical and practical interest. They have been investigated as precursors to aluminum nitride,[1,2] and they have been examined for catalytic activity.[3] The bonding in these compounds can be seen as a mixture of normal and dative bonding, and multiple bonds and even some aromaticity are possible.[4] As an important part of aluminum chemistry, these compounds have been reviewed recently.[5,6] Advances continue to be made in the synthesis of rings with three-coordinate Al and N. The first was the six-membered ring synthesized by Waggoner et al.[7] Very recently four-membered rings with three-coordinate Al and N were synthesized by Fisher et al.,[8] by Schulz et al.,[9] and by Wehmschulte and Power.[10] The analysis of elementary Al−N bonding in small molecules has only recently been undertaken,[11,12] and many questions remain, in particular concerning the structure and stability of possible Al−N double bonds. These questions are of interest theoretically but also synthetically in conjunction with Al−N cluster compounds, their precursors, and their possible decomposition products.

Synthesis of Al−N clusters begins with the monomeric adducts related to $R_3Al{:}NR'_3$. An example is the dimerization of $Me_3Al{:}N(H)Me_2$, which, when heated eliminates $2CH_4$ to form the four-membered ring compound $[Me_2Al-NMe_2]_2$.[13,14] The crystal structure of this compound was reported in the early 1970s.[15,16] Four-membered rings of the general formula $[Me_2Al-NHR]_2$ are in turn the starting point for a series of clusters with the general formula $[MeAl-NR]_n$. In general, the smaller the R group the greater the tendency to form larger clusters. There is apparently a strong drive for elimination of alkane and formation of extended Al−N structures. When R = $Ph(Me)_3$, a cube compound of formula $(MeAl-NR)_4$ is formed.[17] All of the compounds of formula $[RAl-NR']_n$ except the rings mentioned above are clusters that retain four-coordinate nitrogen and aluminum.

Although much has been done from a practical perspective, we wish to assess the nature of the Al−N bond in these compounds. Although the six-membered ring is not aromatic,[4] the double bonds are apparently structurally important, and the bond lengths are similar to those of the double bonds found in small model compounds.[12] The lack of aromatic stabilization of the six-membered ring should mean the lack of antiaromatic destabilization in the four-membered cyclobutadiene analogues. We wish to further the study of both the known Al−N clusters and rings that possess four-coordinate Al and N, and to extend the study of Al−N double ("normal" covalent + dative) bonds.

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We will present results for the four-membered ring model compounds $[H_2Al-NH_2]_2$ and $[HAl-NH]_2$, and the cube tetramer $[HAl-NH]_4$. We will present optimal geometries and theoretical harmonic vibrational frequencies, and compare theoretical results to experiment. On the basis of earlier results we will also be able to present energies of formation of the ring compounds from monomers, and energies of hydrogenation of the unsaturated ring, and the energy of formation of the prototypical cube.

Theoretical Methods

Ab initio theoretical studies were carried out initially at the Hartree−Fock self-consistent field (SCF) level using a double-ζ plus one set of polarization functions (DZP) basis set. The Huzinaga−Dunning (9s5p/4s2p) basis set[18,19] was used for nitrogen, and the (4s/2s) basis set was used for hydrogen. For aluminum the Huzinaga−Dunning (11s7p/6s4p) basis set[20,21] was used. The polarization function orbital exponents were Al = 0.40, N = 0.80, and H = 0.75. Electron correlation was included via the method of configuration interaction including all single and double excitations (CISD), and the coupled cluster method, including all single and double excitations (CCSD). In all correlated methods the orbitals corresponding to the Al and N 1s atomic orbitals were frozen and the corresponding high-energy virtual orbitals were deleted. A larger basis set was also used at the SCF and CISD levels to ensure that no anomalous results were obtained due to basis set size. A triple-ζ basis set plus two sets of polarization functions (TZ2P) consisting of the Huzinaga−Dunning[18,22] (10s6p/5s3p) basis set on N, and (5s/3s) basis set on H, and the McLean−Chandler[20,23] (12s9p/6s5p) basis set on Al, plus polarization functions with exponents of 0.80 and 0.20 for Al, 1.60 and 0.40 for N, and 1.50 and 0.375 for H. Geometry optimizations were all performed via analytic first derivative methods. Harmonic vibrational frequencies were obtained via analytic second derivatives for the SCF method, and by finite difference of analytic first derivatives for the CISD and CCSD methods. The PSI suite of programs was used throughout.[24]

Results and Discussion

Optimized geometries of the four-membered $(AlH-NH)_2$ ring at various levels of theory are given in Figure 1. The vibrational frequencies of this ring are given in Table 1. The theoretical results for the $(AlH_2-NH_2)_2$ ring are given in Figure 2 and Table 2, and the results for the $(AlH-NH)_4$ cube are given in Figure 3 and Table 3. The total energies of the various molecules are given in Table 4. We will first discuss the structures and spectra of the rings and analyze their implications for Al−N bonding. We will then examine the cube structure and spectrum and finally assess the energetics of various reactions.

$(HAl-NH)_2$. The structure of the unsaturated ring is of particular interest because of the presence of Al−N double ($\sigma + \pi$ donation) bonds. As mentioned above unsaturated rings have only recently been synthesized, and until recently very few unassociated aluminum amides with three-coordinate Al and N been had been synthesized.[25−27] The experimental Al−N bond lengths for the four-membered rings are 1.824 Å for the ring synthesized by Wehmschulte and Power,[10] 1.811 Å for the ring of Schulz et al.,[9] and 1.804 (average) for the ring of Fisher et al.[8] The ring synthesized by Schulz et al. also had exocyclic Al−N bonds that would affect the ring π system; therefore, the best comparisons for theory are the values of 1.824 and 1.804 Å. The second is nearly identical to the theoretical value of 1.803 Å (DZP CCSD). The unassociated aluminum amide of the form $(R_2N)_2AlR'$, where R = $(SiMe_3)_2$ and R′ is 2,4,6-

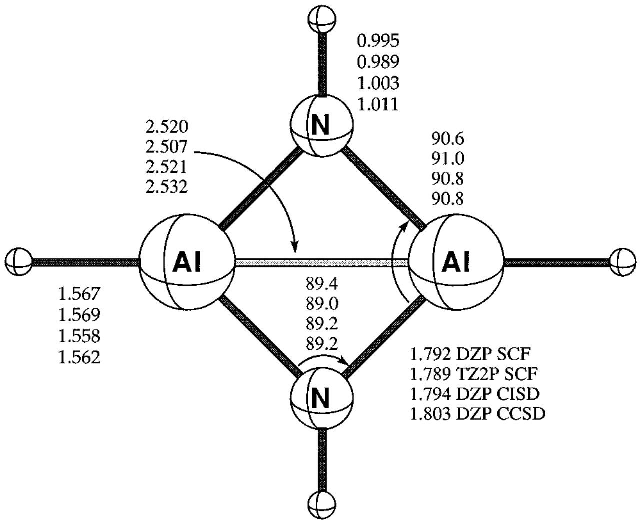

Figure 1. Theoretical geometries in ångströms and degrees at various levels of theory for the $(HAl-NH)_2$ ring.

Table 1. Vibrational Frequencies for the $(H-Al-N-H)_2$ Ring at Various Theoretical Levels[a]

mode (IR intens. in km mol^{-1})	SCF	CISD
A_g		
N−H str (0)	3918/3919	3848
Al−H str (0)	2054/2040	2075
ring breath (0)	895/888	883
ring def (0)	514/516	503
B_{1g}		
bend (N−H) (0)	959/927	931
str (0)	715/711	709
bend (Al−H) (0)	599/594	587
B_{2g}		
N−H in plane bend (0)	491/438	438
B_{3g}		
Al−H in plane bend (0)	529/526	515
B_{1u}		
N−H bend (467)	632/606	600
Al−H bend (246)	558/554	539
ring pucker (2)	250/233	230
B_{2u}		
Al−H str (487)	2045/2030	2072
bend (451)	995/961	1221 (str)
str (161)	784/778	881 (bend)
B_{3u}		
N−H str (90)	3920/3920	3848
str (552)	912/905	904
bend (97)	623/616	617

[a] Notation is DZP/TZ2P; if only one number is given, it was obtained with the DZP basis set. IR intensities were obtained at the DZP SCF level.

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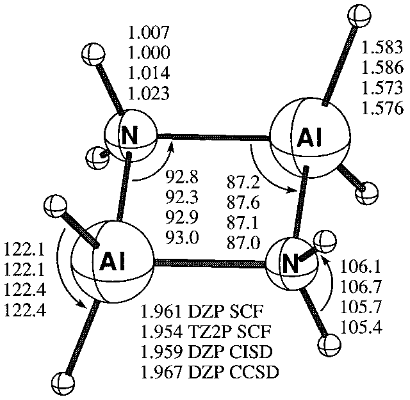


Figure 2. Theoretical geometries in ångströms and degrees at various levels of theory for the $(H_2Al-NH_2)_2$ ring.

Table 2. Vibrational Frequencies for the $(H_2AlNH_2)_2$ Ring at Various Theoretical Levels[a]

mode (IR intens. in km mol^{-1})	SCF	CISD
A_g		
NH str (0)	3724/3727	3660
AlH str (0)	1998/1971	2022
HNH bend (0)	1722/1732	1662
HAlH bend (0)	845/832	836
ring breath (0)	625/626	623
ring def. (0)	361/363	352
B_{1g}		
NH_2 wag (0)	961/934	933
AlH_2 wag (0)	699/690	689
ring def. (0)	468/472	475
B_{2g}		
NH str (0)	3796/3792	3735
AlH_2 twist (0)	681/674	668
NH_2 rock (0)	491/493	481
B_{3g}		
AlH str (0)	1980/1949	2012
NH_2 twist (0)	912/911	897
AlH_2 rock (0)	408/399	396
A_u		
NH_2 twist (0)	871/868	856
AlH_2 twist (0)	476/472	467
B_{1u}		
NH str (72)	3796/3792	3735
AlH str (607)	1985/1954	2017
NH_2 rock (254)	805/796	786
AlH_2 rock (32)	440/439	428
ring flop (28)	107/109	102
B_{2u}		
AlH str (267)	1986/1959	2012
NH_2 wag (769)	962/936	934
AlH_2 scis. (472)	808/791	798
ring def. (70)	553/553	553
B_{3u}		
NH str (67)	3724/3728	3659
NH_2 scis. (146)	1713/1721	1651
AlH_2 wag (874)	823/813	814
ring def. (0)	546/547	546

[a] Notation is DZP/TZ2P; if only one number is given, it was obtained with the DZP basis set. IR intensities were obtained at the DZP SCF level.

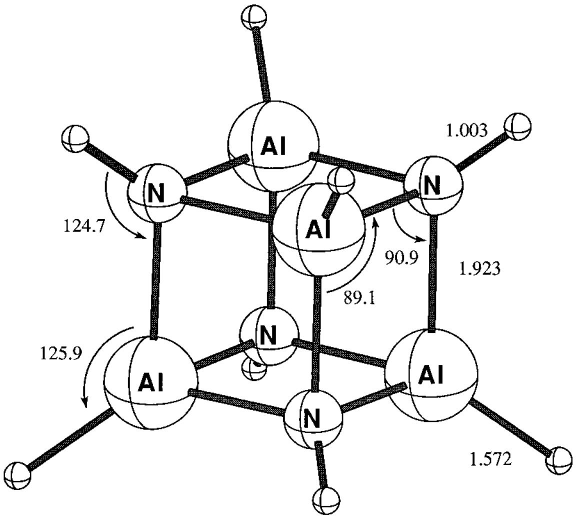


Figure 3. Theoretical geometry in ångströms and degrees for the $(HAl-NH)_4$ cube at the DZP SCF level.

Table 3. Theoretical Vibrational Frequencies in cm^{-1} for the $(HAl-NH)_4$ Cube at the SCF Level[a]

mode (IR intens. in km mol^{-1})	DZP basis	DZ basis
A_1		
N−H str (0)	3822	3836
Al−H str (0)	2033	2004
Al−N str (0)	789	788
cube angle def (0)	548	568
E		
N−H wag (0)	927	1068
Al−H wag + Al−N str (0)	651	652
Al−H wag + Al−N str (0)	493	491
cube angle def (0)	323	344
T_1		
N−H wag + cube angle def (0)	867	1020
HAlN bend + cube twist (0)	588	591
Al−N str (0)	477	485
T_2		
N−H str (159)	3823	3837
Al−H str (1131)	2019	1988
HNAl bend (2181)	938	1070
cube AlNAl bend + HAlN bend (1530)	796	780
cube NAlN bend (294)	672	671
HAlN bend + cube AlNAl def (81)	541	537
cube angle def (3)	373	406

[a] IR intensities were obtained at the DZP SCF level.

Table 4. Total Energies in Hartrees of Optimized Structures at Various Levels of Theory

molecule and basis	SCF	CISD	CCSD
$(HAl-NH)_2$			
DZP	−595.182 117	−595.792 874	−595.888 423
TZ2P	−595.229 503		
$(H_2Al-NH_2)_2$			
DZP	−597.540 638	−598.198 371	−598.310 847
TZ2P	−597.588 841		
$(HAl-NH)_4$			
DZP	−1190.547 884		

trimethylbenzene, has an Al−N bond length of 1.807 Å (average).[25] Steric hindrance may have an effect in these molecules. Comparison with the unassociated compound is also complicated because the aluminum and nitrogen centers are planar, but the planes are rotated relative to each other, disallowing π interactions (Brothers et al. point out that this rotation shows the greater relative importance of relieving steric repulsions versus maintaining π bonds).[25] It is important to note that despite the difference in groups attached to Al and N, the bond length obtained theoretically is quite close to experiment for these three-coordinate bonds, which implies a strong dependence of bond length on coordination number, with a weak dependence on π interactions superimposed.

Theoretical results can be compared for compounds with three-coordinate Al and N to assess electronic affects only, apart from steric effects. The Al−N bond lengths of the unassociated amide H_2Al-NH_2,[12] the four-membered ring $(HAl-NH)_2$, and the six-membered ring $(HAl-NH)_3$ at comparable levels of theory (DZP SCF for the first two, 6-31G* SCF for the third[4]) are 1.763, 1.792, and 1.781 Å, respectively. Lyman et al.[28] studied H_2Al-NH_2 by means of generalized valence bond (GVB) wave functions and found an Al−N bond length of 1.78 Å. Because GVB wave functions include antibonding character, they usually give longer bond distances than the SCF method, and thus the results of Lyman et al. are not inconsistent with ours. The increase from the unassociated compound to the rings can be attributed to either the presence of a full π interaction in the unassociated compound, versus only a partial π interaction in the ring, or to the presence of two Al−N bonds at each center in the rings. Brothers et al. find, however, that Al−N bond lengths tend to decrease with the number of Al−N bonds, i.e., $R_2Al-NR'_2$ longer than $RAl-(NR'_2)_2$ longer than $Al(NR_2')_3$. The shorter bond length in the unassociated compound could be due to the full π interaction. The difference in theoretical bond lengths for the four-membered versus the six-membered rings mirrors that found experimentally. As pointed out by Wehmschulte and Power,[10] the narrow bond angles required by the four-membered ring would tend to increase the p character of the Al−N bonds in that ring, making them longer. At each level of theory the ring Al−N is about 0.03 Å longer than that of H_2Al-NH_2;[12] and both the N−H and Al−H bonds shorten slightly. This, too, can be explained by the constraint of approximately 90° ring angles, as the p orbital character in the ring bonds increases, which lengthens these bonds, the s orbital character in the Al−H and N−H bonds must increase, which shortens these bonds (compared to H_2Al-NH_2).

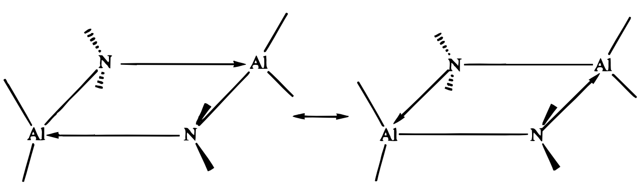
Haaland[5] has used the modified Schomaker−Stevenson rule to give an estimated value of 1.82 Å for a “normal” Al−N bond involving a three-coordinate Al atom. This “normal” bond is one that (in this case) yields neutral radicals upon breaking, as opposed to a dative bond which would yield either neutral closed shell species, or radical ions. The estimated value could be in the range of 1.79−1.85 Å depending on the correction used for ionic factors. The theoretical results for the four-membered ring falls in this range, but the unassociated compound and the six-membered ring do not.

Both experimentally and theoretically the rings are planar with D_{2h} symmetry. The donation of electrons from the electropositive Al to N decreases the energy required to change the normally sp[3] lone pair to a p orbital lone pair in the planar species. Thus the nature of the Al−N σ bond allows planarity, which in turn allows the π interaction. The Al−Al distance in this ring is quite short. However, neither Mulliken overlap populations nor the force constant matrix indicates any bonding. When the second-derivative matrix was evaluated for an Al−Al stretch, the diagonal matrix element was small and the off-diagonal elements were large. The short Al−Al distance appears to be a result of the angle constraints of the planar four-membered ring.

The ring stretching modes of $(AlH-NH)_2$ are clustered around 900 cm^{-1}, with an intense b_{3u} mode at 904 cm^{-1} (at the DZP CISD level). This is close to the value of 876 cm^{-1} found theoretically for the Al−N bond in H_2Al-NH_2 and also close to the value of 900 cm^{-1} found for solid AlN.[23] The lowest frequency mode, which corresponds to the butterfly motion of the ring, is at 230 cm^{-1}.

$(H_2Al-NH_2)_2$. Rings composed of four-coordinate Al and N are common and well characterized. The geometry of the model compound is, at all theoretical levels, nearly identical to that found experimentally for the $(Me_2Al-NMe_2)_2$ ring.[16] The $(Me_2Al-NMe_2)_2$ ring has an Al−N bond length of 1.96 Å and an Al−N−Al angle of 92° compared to 1.959 Å and 92.9° for $(AlH_2-NH_2)_2$ at the DZP CISD level and 1.967 Å and 93.0° at the DZP CCSD level.

Scheme 1



The vibrational frequency for the ring butterfly motion is only 102 cm^{-1} in the saturated $(AlH_2-NH_2)_2$ ring. This is consistent with the loss of whatever weak π interaction is present in $(AlH-NH)_2$ but is probably due in part to the longer, weaker σ bonds in $(AlH_2-NH_2)_2$. As pointed out by Haaland[5] the σ bonds in the saturated ring can be viewed as half-and-half combinations of normal and dative bonds (Scheme 1) and would be expected for this reason to be a floppier molecule than the unsaturated ring. The Al−N ring stretching frequencies also decreased compared to the $(HAl-NH)_2$ ring. The mode with the largest IR intensity is at 553 cm^{-1} with the DZP CISD method. This is close to the Al−N stretching frequency of 508 cm^{-1} found by Beachly et al. for $(Me_2Al-NMe_2)_2$.[29]

The Al−H and N−H stretching frequencies of the saturated ring are lower than those of the unsaturated ring, but higher than those of free AlH_3 and NH_3, respectively. Formation of the H_3Al-NH_3 dative bond causes a lengthening and weakening of both Al−H and N−H bonds as electron donation from N to Al occurs.[11] In both the $(HAl-NH)_2$ and the $(H_2Al-NH_2)_2$ rings, the Al−H and N−H bonds shorten compared to those of AlH_3 and NH_3, respectively. This is consistent with electron flow from Al to N, opposite that of the dative bond in H_3Al-NH_3.

$(HAl-NH)_4$. The computational demands of the cube structure deterred investigation at the CISD or CCSD levels. The results on the rings, however, are consistent across all theoretical levels. It is clear that the systems with four-coordinate Al and N are well described at the DZP SCF level, and comparison shows that reasonable results are obtained with the even smaller DZ basis set. The theoretical results at the SCF/DZP level for the cube are in good agreement with experimental values for $[MeAl-N(i\text{-}Pr)]_4$: our theoretical Al−N bond length is 1.923 Å, and the experimental bond length is 1.92 Å.[30] It is reasonable that the bond length of the cube is less than that of the $(H_2Al-NH_2)_2$ ring. In the ring each Al−N bond is the average of a normal covalent bond and a dative bond, but in the cube each Al−N bond is the average of two normal covalent bonds and a dative bond. The Al−N distance in aluminum nitride is 1.89 Å, only slightly shorter than the cube.

The high symmetry of the cube (T_d) makes the theoretical IR spectrum particularly simple. Three very intense bands are predicted. If we apply the usual scale factor of 10% for SCF frequencies, these intense absorptions are expected to appear at 1816, 844, and 716 cm^{-1} and correspond to an Al−H stretch, an Al−N−H bend, and an Al−Al−H bend, respectively.

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The Al−H and N−H stretching frequencies in the cube are lower than those of the unsaturated $(HAl{-}NH)_2$ ring, but are higher than those of AlH_3 and NH_3 respectively. Formation of the $H_3Al{-}NH_3$ dative bond causes a lengthening and weakening of both Al−H and N−H bonds as electron density is transferred from N to Al.[11] In both rings and the cube, the Al−H and N−H bonds shorten compared to AlH_3 and NH_3, consistent with flow of electron density from Al to N. The Mulliken charge separation between Al and N is largest for the cube compound, with Al = +1.4 and N = −1.4.

Reaction Energies. The overall reaction scheme begins with a Lewis acid−base complex and ends in a cluster, and conceptually it can be broken into two cycles of (a) hydrogen elimination and (b) dimerization, as is shown in Figure 4. The hydrogen elimination part of the cycle forms an intermediate that is higher energy than the starting material, and the dimerization part forms the low-energy product and thus provides the energy payoff. The energy of the hydrogen elimination step is of interest because it gives a clue to the mechanism; a very high energy implies that the reaction does not proceed by simple hydrogen loss. The energy of the dimerization step indicates the strength of the overall driving force for the reaction. We will therefore look at each step separately.

We use the results of the previous study of Davy and Jaffrey for step 1a of Figure 4. They estimated the energy of this hydrogen loss to be only +4 kcal/mol.[12] From the present study the energy of dimerization of $H_2Al{-}NH_2$ to form the four-membered ring (step 1b in Figure 4) is estimated to be between −55 and −60 kcal/mol at all levels of theory. (DZP SCF = −55 kcal/mol, DZP CISD = −60 kcal/mol, DZP CCSD = −58 kcal/mol. All include ZPVE, but not basis set superposition corrections.) In $H_2Al{-}NH_2$ the Al−N interaction can be considered a normal σ bond plus a dative π bond. Dimerization to form the $(H_2Al{-}NH_2)_2$ ring therefore converts two normal σ plus two dative π bonds to two normal σ plus two dative σ bonds. On a simple view dimerization is conversion of two π dative bonds to two σ dative bonds, and the energy of dimerization is

$$2[E(\sigma\text{ bond})] - 2[E(\pi\text{ bond})]$$

From theoretical studies of Jungwirth and Zahradnik the energy of the σ dative bond between AlH_3 and NH_3 is approximately −30 kcal/mol (allowing for ZPVE correction but neglecting basis set superposition error).[31] Thus, on a simple view, the dimerization energy is provided by the formation of two σ dative bonds, with negligible energy increase due to loss of the two π dative bonds.

Unlike the small energy requirement for hydrogen loss from $H_3Al{-}NH_3$, hydrogen loss from the $(H_2Al{-}NH_2)_2$ ring to form the $(HAl{-}NH)_2$ ring requires 42.5 kcal/mol (DZP CCSD including ZPVE correction). The energy of dimerization of $(HAl{-}NH)_2$ to form the $(AlH{-}NH)_4$ cube is −111.7 kcal/mol at the DZP SCF level; thus the overall energy for the reaction

$$2(H_2Al{-}NH_2)_2 \rightarrow (HAl{-}NH)_4 + 4H_2$$

is found theoretically to be −27 kcal/mol.

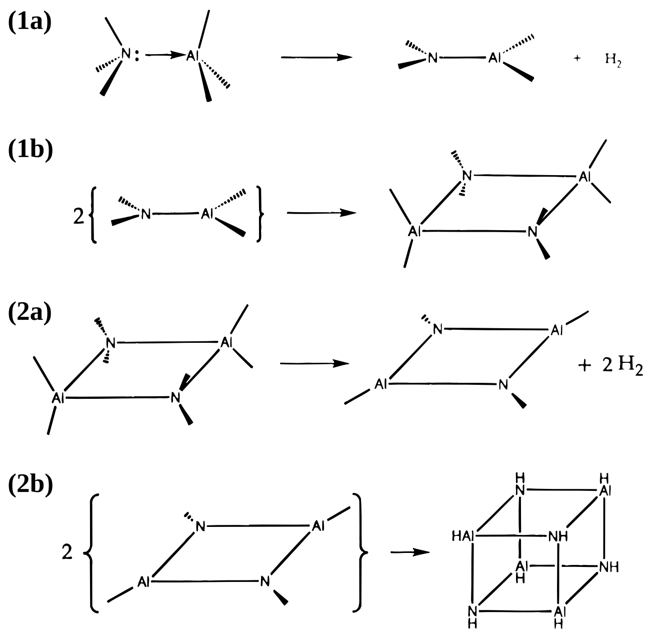
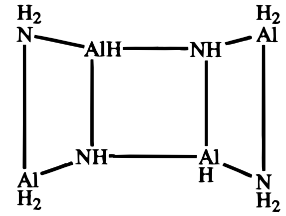


Figure 4. Conceptual outline for the formation of the $(HAl{-}NH)_4$ cluster beginning with the $H_3Al{-}NH_3$ adduct. Each overall step is broken down into a hydrogen elimination and a dimerization.

Gorling and Bowen found that alkane elimination and dimerization of a Lewis acid−base complex to form an $(R_2Al{-}NR_2)_2$ ring was surface catalyzed.[32] Clearly the subsequent alkane loss from the ring and dimerization to form the cube, a process that requires substantially more energy for the initial elimination, would need to be either catalyzed or concerted. Gorling and Bowen postulated the initial attachment of an edge.



This would allow intermolecular loss of hydrogen, and avoid the unsaturated ring as an intermediate, which we find to be high in energy.

Conclusions

The $(AlH{-}NH)_2$ ring is found theoretically to be planar with Al−N bond lengths shorter than those of a "normal" (i.e. not dative) Al−N bonds. The planarity does not imply significant π interaction. The nitrogen atom remains planar due to the large Al to N charge transfer, and the planar nitrogen allows some π back-donation to the aluminum. Comparison of theoretical geometries of the model compound and the experimental geometry of recently synthesized rings shows that in the absence of steric repulsions the Al−N bond lengths are quite short. The energy required to lose hydrogen from the $(AlH_2{-}NH_2)_2$ ring in order to form the $(HAl{-}NH)_2$ ring is quite high (~42 kcal/mol) and suggests that loss prior to formation of the cubic cluster requires the involvement of another ring. In contrast hydrogen elimination from $H_3Al{-}NH_3$ to form the $(H_2Al{-}NH_2)_2$ ring requires only about 8 kcal/mol per ring. Infrared spectra for these rings and cluster are predicted to have high-intensity bands.

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