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Thermochemical properties of molecules and cations of MgN_nH_m ($n = 1, 2$ and $m = 1–6$) : enthalpies of formation, proton affinities and ionization energies

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Abstract

Ab initio molecular orbital calculations are reported for small neutral molecules and cations containing magnesium, nitrogen and hydrogen. Structures have been optimized using gradient techniques at B3LYP/6-31+G(d) and at MP2(full)/6-311++G(d,p). Single-point calculations are reported at QCISD(T)(full)/6-311++G(2df,p) and at CCSD(T)(full)/6-311++G(2df,p) levels using geometries optimized at MP2(full)/6-311++G(d,p). Standard enthalpies of formation at 298 K have been calculated at these two higher levels of theory. Other thermochemical properties calculated include ionization energies and proton affinities. The binding enthalpies of ammonia to Mg^+, $MgNH_2^+$ and $MgNH_3^+$ are also reported. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: MgN_nH_m; Thermochemical properties; Ab initio calculations

1. Introduction

Magnesium-containing compounds have recently attracted considerable attention in astrochemistry. Metals have low ionization energies and recombine only slowly with electrons and therefore they are likely to exist in singly ionized form [1]. Laboratory studies have also shown that metallic ions can react via radiative association processes and so lead to the formation of interstellar molecules containing metallic elements [2].

The only magnesium-containing molecules identified by radioastronomy are the radicals MgNC and MgCN in the outer envelope of IRC+10216 by Guèlin and his coworkers in 1986 [3,4]. To our knowledge, there have been no reports of molecules $MgNH_n$ existing in interstellar media; however, the gas-phase chemistry of ion $MgNH_3^+$ has been investigated in the laboratory [5,6] and a proposal has been made for the circumstellar formation of $MgNH_2$ [5]. The results of the recent measurements of the kinetics for the sequential ligation of ammonia to Mg^+ were interpreted in terms of a change from direct coordination to the metal center to solvation of a ligated ammonia molecule [5]. A theoretical investigation of $Mg(NH_3)_n^+$, where $n = 0$ to 4, provided structural information and binding energies for the directly ligated ions and also for the solvated ions.

Bauschlicher's group undertook a theoretical study [7] of the positive and dipositive ions of $Mg(NH_3)_n$ where $n = 0$, to 3, and found a good agreement with the available experimental data. Their results provided accurate experimental metal-ion–ligand binding energies, but very little structural information

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Table 1
Total energies, zero-point and thermal energies from structural optimizations

Molecule	BeLYP[a] (hartrees)	MP2[b] (hartrees)	ZPE[c] (kcal mol^{-1})	Thermal (kcal mol^{-1})	QCI[d] (hartrees)	CCSD(T)[e] (hartrees)
$MgNH^+$ ($^2A''$)	−255.08051	−254.64701	7.1	2.0	−254.70625	−254.70593
MgNH ($^1A'$)	−255.33348	−254.90725	6.4	1.9	−254.97414	−254.97234
MgNH ($^3\Pi$)	−255.34498	−254.91200	6.6	2.0	−254.97343	−254.97317
$MgNH_2^+$ ($^1A_1$)	−255.76031	−255.33719	14.2	2.1	−255.39569	−255.39532
$MgNH_2$ ($^2A_1$)	−256.02572	−255.59419	13.6	2.4	−255.65395	−255.65367
$MgNH_3^+$ ($^2A_1$)	−256.41900	−255.98947	22.6	2.2	−256.04506	−256.04491
$Mg(NH_3)_2^+$ ($^2A_1$)	−313.02586	−312.47396	45.3	4.3	−312.58008	−312.57981
$Mg(NH_2)_2$ ($^1A_1$)	−312.03331	−311.48786	28.2	4.1	−311.59748	−311.59702
$H_2NMgNH_3^+$ ($^1A'$)	−312.41069	−311.86739	37.1	4.2	−311.97502	−311.97463
$MgNH_2^+\cdots(NH_3)$ (^1A)	−312.33811	−311.79068	36.6	4.1	−311.89780	−311.89721
NH_3 ($^1A_1$)	−56.55699	−56.43468	20.6	1.8	−56.48412	−56.48399
Mg (^1S)	−200.07958	−199.75739	–	0.9	−199.77368	−199.77364
Mg^+ (^2S)	−199.79555	−199.49146	–	0.9	−199.49597	−199.49594
N (^4S)	−54.58777	−54.49533	–	0.9	−54.53134	−54.53132
H (^2S)	−0.50027	−0.49982	–	0.9	−0.49982	−0.49982
H_2 ($^1\Sigma_g^+$)	−1.17548	−1.16030	6.4	1.5	−1.16836	−1.16838

[a] Optimization at B3LYP/6-31+G(d).

[b] Optimization at MP2(full)/6-311++G(d,p).

[c] Zero-point energies are scaled by 0.94.

[d] Single-point at QCISD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p).

[e] Single-point at CCSD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p).

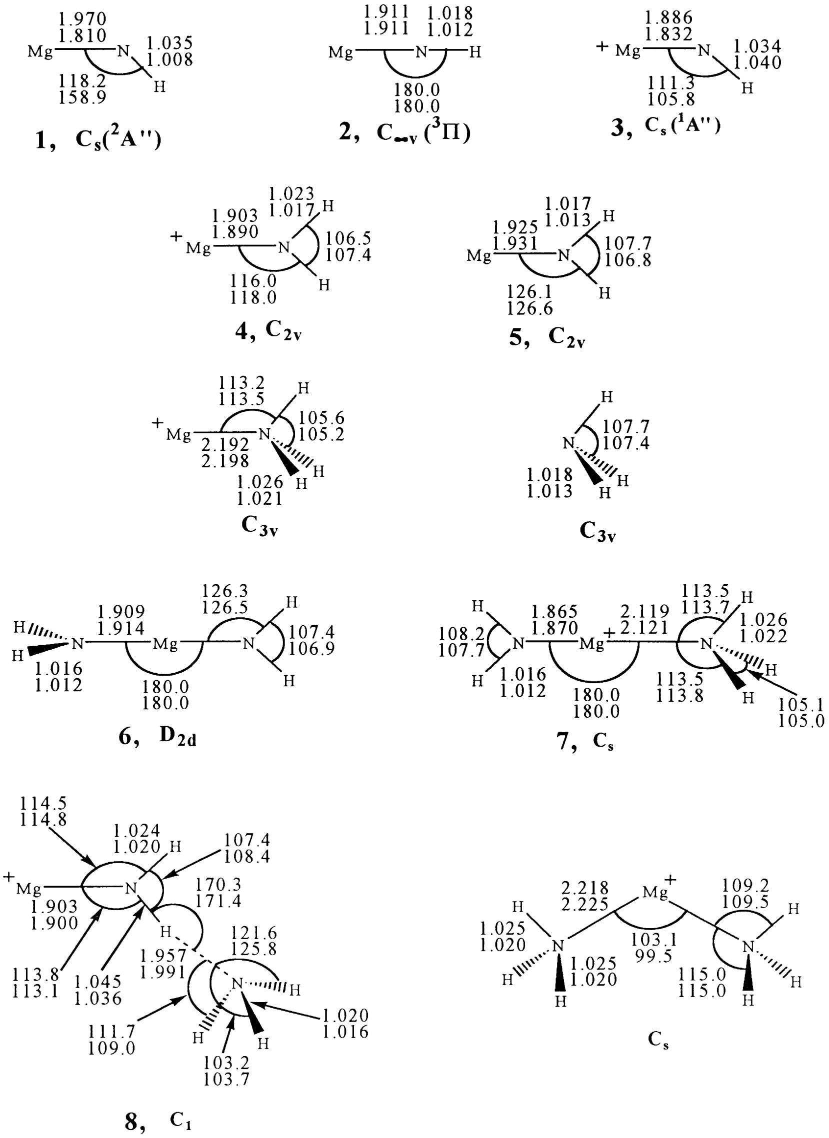


Fig. 1. Optimized structures at B3LYP/6-31+G(d) (top numbers) and MP2(full)/6-311++G(d,p) (bottom numbers).

[7]. Our theoretical analysis of these small systems provides structural details to complete the picture [5,6]. The overall conclusions of the theoretical studies are all in good agreement.

The gas-phase ion chemistry of magnesium was also the focus of a recent paper that provided the thermochemical properties for MgO_nH_m, neutrals and ions [8]. The study by Goodings and his coworkers [8] used experiments to probe the chemistry of magnesium ion in fuel rich H_2–O_2–N_2 flames at atmospheric pressures in the temperature range 1820–2400 K and employed ab initio calculations to assess the validity of the experimental results at the QCISD(T)(full)/6-31++G(2df,p) and CCSD(T)(full) /6-311++G(2df,p) levels of theory. A survey of literature enthalpies, both experimental and theoretical, revealed considerable scatter and Goodings' study provided the first fully consistent set of enthalpies for MgO_nH_m ions and molecules. The current work reports calculations on the magnesium–nitrogen–hydrogen compounds, MgN_nH_m, using the same levels of theory as for MgO_nH_m and, as there are no literature values available for this family, the aim of the current study is to provide the first reliable thermochemical properties for cations and molecules of this composition.

2. Computational details

Standard ab initio molecular orbital calculations were performed using the GAUSSIAN 94 program [9]. Geometries were optimized using the gradient techniques [10–12] at MP2(full) with a 6-311++G(d,p) [13–20] basis set, denoted MP2, and at B3LYP [20–25] with a 6-31+G(d) basis set, denoted B3LYP. The optimized structures were characterized by harmonic frequency calculations, which showed them all to be at minima, i.e. all structures had no imaginary frequencies. The frequency calculations also provided the zero-point energies and thermal corrections that were used to calculate the standard enthalpies of formation and other thermochemical properties at 298 K. The zero-point energies from the MP2 frequency calculations were scaled by a factor of 0.94 [26]. Single-point calculations were also performed at QCISD(T)(full) [27] and CCSD(T)(full) [28–31] with a 6-311++G(2df,p) basis set [32] using the geometries optimized at the MP2 level. The total energies, ground state electronic configurations scaled zero-point energies and thermal corrections from these calculations are given in Table 1.

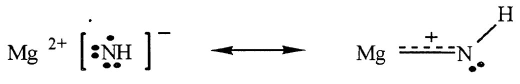
3. Results and discussion

3.1. Structural details

Details of structures as calculated at B3LYP (upper numbers) and MP2 (lower numbers) are given in Fig. 1. For most structures there is an excellent agreement between the two levels of theory and, for the sake of clarity where this is the case, we use only the MP2 structures in the discussion.

3.1.1. $MgNH^+$ (*1*)

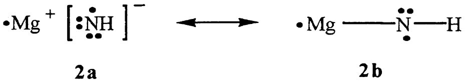
At both B3LYP/6-31+G(d,p) and MP2(full)/6-311++G(d,p) *$MgNH^+$* is bent and has one valence electron in the π-system, essentially localized in the π-orbital on N, formally leaving a positive charge on Mg (the calculated charge from a Mulliken population analysis on Mg is +1.02). Perhaps the best description of this ion is as an ionic bond, as shown in structure **1a**, with some contribution from covalent structure **1b**. There are, however, large differences in the geometries calculated for this ion at different levels of theory. At B3LYP/6-31+G(d,p) the Mg–N distance is 1.970 Å, whereas at MP2(full)/6-311++G(d,p) it is 1.810 Å; the bond angles also differ greatly, 118.2° at B3LYP/6-31+G(d,p) and 158.9° at MP2(full)/6-311++G(d,p). In an attempt to resolve this problem we carried out optimizations at B3LYP/6-311++G(2d,p) and at CCSD(T)(full)/6-311++G(2df,p) and obtained very similar structures, a linear ion with Mg–N distances of 1.815 and 1.812 Å, respectively. Clearly these parameters are in much closer agreement with those from the lower level MP2 calculations and the energies for these structures were essentially the same as those obtained using the MP2(full)/6-311++G(d,p) optimized structure.



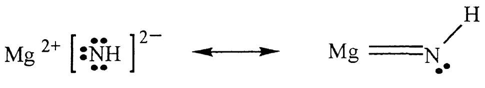
1 a **1 b**

3.1.2. MgNH (**2** *and* **3**)

The singlet and triplet states of MgNH have similar energies. At lower levels of theory the triplet has the better energy (when zero-point and thermal energies are included, by 6.9 kcal mol^{-1} at B3LYP/6-31++G(d,p) and by 2.7 kcal mol^{-1} at MP2(full)/6-31++G(d,p)). However, single-point calculations at higher levels show the two states to be within less than 1 kcal mol^{-1} of each other (at QCI the singlet is preferred by 0.7 kcal mol^{-1}, whereas at CCSD(T) the triplet has the better energy by 0.2 kcal mol^{-1}). The geometries of the molecule in these two states are quite different. The molecule in the triplet state is linear with one unpaired electron in the σ-system located on Mg and the other in an unequally-filled set of π-orbitals. The Mg–N distance of 1.911 Å is 0.101 Å longer than that in MgNH$^+$ and is essentially a Mg–N single bond. This structure is best represented by resonance between ionic structure **2a** involving two singly charged ions and covalent structure **2b**.

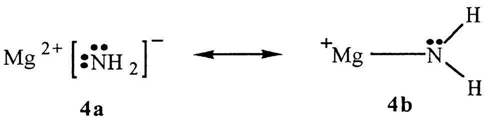

2a **2b**

MgNH in the singlet state has a bond angle of 105.8°, considerably smaller than that characteristic of an sp^2 hybridized center. The bond distance is considerably shorter than that in the triplet, but is dependent on the level of theory used, having distances of 1.886 Å at B3LYP/6-31+G(d,p) and 1.832 Å at MP2(full)/6-311++G(d,p) i.e. as with MgNH$^+$, the B3LYP calculation gives a much larger bond length than MP2. Overall, the structure is probably the best described as an intermediate between an ionic structure with an interaction involving doubly charged ions (structure **3a**) and a covalent structure containing a double bond (structure **3b**), although the π-electrons are mainly located on the nitrogen.


3a **3b**

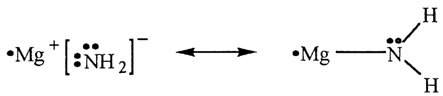
3.1.3. MgNH$_2^+$ (4)

Ion **4** has an Mg–N distance of 1.890 Å, 0.080 Å longer than in ion **1**. The two π-electrons in this structure are essentially localized on the nitrogen. The Mg–N bond distance is slightly longer than that in **3**, i.e. protonation of the lone pair in **3** results in even greater localization of the π-electrons on nitrogen. The charge on magnesium is calculated to be +1.20 and the structure is best represented by resonance structures **4a** and **4b**.


4a **4b**

3.1.4. MgNH$_2$ (5)

Addition of an electron to ion **4** results in **5**, a molecule in which the unpaired spin is localized on the magnesium in the σ-system. Molecule **5** has a longer Mg–N distance than ion **4** (1.931 Å compared to 1.890 Å).

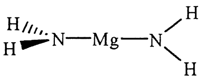

5a **5b**

3.1.5. Mg(NH$_2$)$_2$ (6)

Molecule **6**, H$_2$NMgNH$_2$, is valence isoelectronic with allene and adopts the same structure with the two NH$_2$ groups being in planes that are perpendicular to each other (D_{2d} symmetry). The N–Mg distances in this molecule at 1.914 Å are slightly shorter than that in MgNH$_2$ (1.931 Å).

3.1.6. Mg(NH$_2$)$_2$H$^+$ (7)

Protonation of molecule **6** to form ion **7** results in a shortening of the remaining H$_2$N–Mg distance to 1.870 Å, a distance shorter than that in MgNH$_2^+$ (1.890 Å), while the Mg–NH$_3^+$ distance of 2.121 Å is almost as long as the distance in Mg–NH$_3^+$ (2.198 Å).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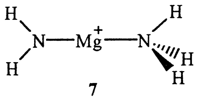
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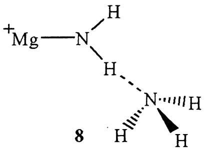
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Table 2
Standard enthalpies of formation at 298 K, ΔH_f° in kcal mol^{-1}

Molecule	QCI[a]	CCSD(T)[b]
$MgNH^+$ ($^2A''$)	263.7	263.9
MgNH ($^1A'$)	91.2	92.3
MgNH ($^3\Pi$)	95.6	95.7
$MgNH_2^+$ ($^1A_1$)	199.0	199.2
$MgNH_2$ ($^2A_1$)	36.6	36.7
$MgNH_3^+$ ($^2A_1$)	164.2	164.3
$Mg(NH_3)_2^+$ ($^2A_1$)	125.2	125.3
$Mg(NH_2)_2$ ($^1A_1$)	−4.1	−3.8
$H_2NMgNH_3^+$ ($^1A'$)	132.5	132.5
$MgNH_2^+\cdots(NH_3)$ (^1A)	180.2	180.5

[a] Single-point at QCISD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p).

[b] Single-point at CCSD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p).

3.1.7. $MgNH_2^+(NH_3)$ (8)

A second isomer of **7**, the solvated ion **8**, is 45–49 kcal mol^{-1} higher in energy than **7**. Ion **8** essentially consists of ion **4** solvated by an ammonia molecule through one hydrogen bond. In **8** the geometries are almost the same as in the separated components, **4** and NH_3. The largest change is in the N–H bond involved in the hydrogen bonding, where complex formation results in an increase from 1.017 to 1.036 Å. The binding enthalpy at 298 K of this complex is almost independent of the level of theory and is 9.8 kcal mol^{-1} at CCSD(T)/6-311++G(2df,p).

3.1.8. $Mg(NH_3)_n^+$

Simple electrostatic bonds formed between NH_3 and Mg^+ are considerably longer (and weaker) than those in the unsaturated $MgNH_n$ molecules and ions. The bond lengths in ions $Mg(NH_3)_n^+$, where $n = 1$–4, are in the range 2.15–2.24 Å [5,6,33] (curiously the tetrahedral $Mg(NH_3)_4^+$ ion has the shortest bond lengths). In $H_3NMgNH_3^+$ the bond angle NMgN is 99.5°, much smaller than the angle at a typical sp^2 hybridized atom. Bauschlicher [33] attributes this to polarization of the 3s orbital away from the ligands. An alternative explanation is that bonding occurs through the donation from the nitrogen lone pairs into two of the vacant p-orbitals of magnesium and steric interaction between the ammonia molecules then causes the angle to open up from 90° [5,6]. When a second ammonia is introduced into the system, the Mg–N bond length increases slightly (from 2.198 to 2.225 Å).

In general, addition of a hydrogen atom to a molecule or ion causes an increases in the Mg–N bond length. The most dramatic examples of this occur in the ions; on going from $MgNH^+$ to $MgNH_2^+$, Mg–N increases by 0.058 Å, while on going from $MgNH_2^+$, to $MgNH_3^+$, this distance increases by 0.308 Å.

4. Thermochemical properties

4.1. Enthalpies of formation

Standard enthalpies of formation calculated from heats of atomization at 298 K are given in Table 2. Previous work has shown that enthalpies of formation using QCISD(T)(full)/6-311++G(2df,p) are within ±3 kcal mol^{-1} of the accepted experimental values [34–38]. The procedure used to calculate the enthalpies of formation of ions and molecules has been detailed previously [36,37,39,40], but a brief description follows. The total atomization energy is calculated from the molecular orbital calculations using an isogyric reaction involving H atoms and H_2 to balance the spins [41–44] and then compensating for the addition of H atoms by using the experimental D_e for H_2 [45]. Inclusion of ZPE then provides D_0 for the molecule. Experimental enthalpies of formation for atoms [46] then enable us to calculate enthalpies of formation for the molecule. Ions are treated in an identical manner, but with a electron being added into the atomization reaction. The stationary electron convention is used. From previous experience, MP2 calculations are at too low a level to give reliable values for enthalpies of formation and for this reason we report only the results from the higher levels of theory. For all the molecules and ions investigated in this study single-point QCI and CCSD(T) calculations are in excellent agreement, with the largest difference being for MgNH (1.1 kcal mol^{-1}).

Neutral molecules have much lower enthalpies of formation than cations, but in both series there is the same trend with the enthalpies decreasing with increasing saturation. The range for the neutral molecules is from 95.7 kcal mol^{-1} for MgNH ($^3\Pi$) to −3.8 kcal mol^{-1} for $Mg(NH_2)_2$. For the ions that have only one nitrogen atom attached to the

Table 3
Proton affinities at 298 K in kcal mol^{-1}

Molecule	B3LYP[a]	MP2[b]	QCI[c]	CCSD(T)[d]
MgNH ($^1A'$)	261.3	263.3	258.0	258.9
$MgNH_2$ ($^2A_1$)	239.5	240.7	238.2	238.2
$Mg(NH_2)_2$ ($^1A_1$)	229.3	230.6	229.4	229.4

[a] Optimization at B3LYP/6-31+G(d).

[b] Optimization at MP2(full)/6-311++G(d,p).

[c] Single-point at QCISD(T)(full)/6-311++G(2df,p)/MP2(full)/6-311++G(d,p).

[d] Single-point at CCSD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p).

magnesium the enthalpies range from 263.9 kcal mol^{-1} for $MgNH^+$ to 164.3 kcal mol^{-1} for $MgNH_3^+$. The solvated ion $MgNH_2^+\cdots NH_3$ has an enthalpy of formation of 180.5 kcal mol^{-1}, and this compares with a value of 199.2 kcal mol^{-1} for the unsolvated ion $MgNH_2^+$. Direct attachment of a second nitrogen to magnesium results in lower enthalpies of formation with ions $Mg(NH_3)_2^+$ and $H_2NMgNH_3^+$ having similar values (125.3 and 132.5 kcal mol^{-1}).

4.2. Proton affinities

The proton affinity of molecule B is defined as the enthalpy change for the removal of H^+ from BH^+ at 298 K, as shown in the following reaction

$$BH^+ \rightarrow B + H^+ \qquad (1)$$

Proton affinities can be calculated reliably at relatively low levels of theory and Table 3 gives values at 298 K in kcal mol^{-1} for MgNH, $MgNH_2$ and $Mg(NH_2)_2$. The calculated proton affinities are similar at all levels of theory, with the MP2 value always being the largest and the order being MP2 > B3LYP > CCSD(T) ≈ QCI. For this property the DFT results agree fairly well with those from the more sophisticated methods employed in this study, QCI and CCSDT. Based on the comparison of proton affinities from experiments and calculations performed at the same levels as employed here but on MgO_nH_m molecules [5], the proton affinities in Table 3 are probably slightly too high, but should be within at least 7 kcal mol^{-1} of the correct value. The first generalization possible from Table 3 is that the proton affinities of the MgN_nH_m molecules decrease with increasing saturation. The same behavior was noted for molecules MgO, MgOH and $Mg(OH)_2$, although the proton affinities of these molecules are lower than those of the isoelectronic MgN_nH_m molecules [8]. The proton affinities of these magnesium–nitrogen molecules are much higher than that of ammonia which on the proton affinity ladder is quite high at 204 kcal mol^{-1} [47,48]. The proton affinities of the magnesium–nitrogen molecules are so large because the nature of the Mg–N bond is altered drastically upon protonation; the Mulliken population on Mg in MgNH ($^1A'$) is +0.46 and this is increased to +1.20 in $MgNH_2^+$, i.e. the majority of the charge introduced by protonation is transferred on to the magnesium atom. The situation is different in the protonation of $MgNH_2$ and $Mg(NH_2)_2$; here the high energy ionic bonds between Mg and N are converted into weaker Mg–N electrostatic bonds. A Mulliken population analysis on $MgNH_2$ shows that the magnesium atom carries a charge of +0.60 and, when protonation on N occurs, the product ion, $MgNH_3^+$, has a charge of +0.73 on magnesium. Here, then, there is

Table 4
Ionization energies at 0 K in eV

Molecule	B3LYP[a]	MP2[b]	QCI[c]	CCSD(T)[d]	Experimental
Mg (^1S)	7.72	7.61	7.72	7.72	7.65 [50], 7.65 [51,52]
$MgNH_2$ ($^2A_1$)	6.90	7.49	7.48	7.39	
$MgNH_2$ ($^3\Pi$)	7.20	7.23	7.29	7.30	
$MgNH_2$ ($^2A_1$)	7.25	7.02	7.06	7.06	

[a] Optimization at B3LYP/6-31+G(d).

[b] Optimization at MP2(full)/6-311++G(d,p).

[c] Single-point at QCISD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p).

[d] Single-point at CCSD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p).

Table 5
Calculated binding enthalpies of $XMg^+–NH_3$ complexes at 298 K (in kcal mol^{-1}) $XMg^+–NH_3 \rightarrow MgX^+ + NH_3$

MgX^+	B3LYP[a]	MP2[b]	QCI[c]	CCSD(T)[d]
Mg^+	40.8	38.8	39.9	39.9
$MgNH_2^+$ (metal coordination)	56.6	57.9	57.7	57.8
$MgNH_2^+$ (solvation)	11.7	10.4	9.9	9.8
$MgNH_3^+$	29.5	29.4	30.1	30.1

[a] Optimization at B3LYP/6-31+G(d).
[b] Optimization at MP2(full)/6-311++G(d,p).
[c] Single-point at QCISD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p).
[d] Single-point at CCSD(T)(full)/6-311++G(2df,p)//MP2(full)/6-311++G(d,p).

relatively little increase in the positive charge carried by the magnesium; nevertheless the metal atom in $MgNH_3^+$ is more effective than a hydrogen atom in NH_4^+ at assisting in carrying the positive charge.

4.3. Ionization energies

The adiabatic ionization energy of a molecule in the gas-phase is defined as the standard enthalpy change of the following reaction at 0 K, assuming that the cation is allowed to relax to its optimum structure. Isogyric reactions involving H and H_2 have been used to minimize differences in correlation energies when calculating the ionization energies given in Table 4.

$$A \rightarrow A^+ + e \qquad (2)$$

There is a good agreement between the calculated ionization energies at different levels of theory. The highest level calculations, QCI and CCSD(T), give essentially the same numbers except in the case of MgNH ($^1A'$) where the QCI value is 0.09 eV higher than that from CCSD(T). The ionization energy for Mg, the only species for which there is an experimental value, is overestimated by 0.07 eV at both QCI and CCSD(T). From the very limited data in Table 4 one trend emerges, the ionization energies decrease as the number of atoms in the molecule increases. This is easily understood in terms of the larger cations being able to more easily accommodate the charge.

4.4. Binding enthalpies

Binding energies calculated from the total energies in Table 1 are listed in Table 5. These do not show much dependence on the level of theory and there is an excellent agreement between the values calculated at the two highest levels. The binding energies calculated for $MgNH_3^+$ and $H_3NMgNH_3^+$ are in good agreement with those reported previously [5,6,49]. One curious feature is that the binding energy of $H_2NMg^+–NH_3$ is 17.9 kcal mol^{-1} higher than that of $Mg^+–NH_3$. This implies that the magnesium atom in the $MgNH_2^+$ ion is more electron deficient than an isolated Mg^+ ion, a feature that can be explained by the presence of the electronegative nitrogen atom giving $MgNH_2^+$ some $Mg^{2+}[NH_2]^-$ character. In keeping with this analysis, the isoelectronic ion $HOMgOH_2^+$ has a binding enthalpy that is 21 kcal mol^{-1} higher than that of $MgNH_2^+$ [8].

5. Conclusions

There is an excellent agreement between the values of all thermochemical properties (proton affinities ionization energies, enthalpies of formation and bond enthalpies) as calculated at the two highest levels of theory, QCISD(T)(full)/6-311++G(2df,p) and CCSD(T)(full)6-311++G(2df,p). The largest discrepancies are for MgNH ($^1A'$), where the two levels of theory give enthalpies of formation that differ by 1.1 kcal mol^{-1}, ionization energies that differ by 0.09 eV, and proton affinities that differ by 0.9 kcal mol^{-1}.

Some calculated properties are worthy of comment.

1. The ionization energy of Mg is the one property for which there is an experimental value and here theory produces a value that is 0.07 eV too high.
2. The proton affinities of the three compounds given in Table 3 are very high and this can be attributed

to the ability of the magnesium to carry much of the positive charge in the cations. The proton affinities decrease as the number of atoms in the base increases.

3. For all the species, the enthalpies of formation as calculated at QCI, are lower than those from the CCSD(T) calculations but, apart from the calculations of MgNH ($^1A'$), the largest difference is only 0.3 kcal mol^{-1}.
4. The binding enthalpy of Mg–NH_3^+ is greater than that of $(NH_3)Mg^+$–NH_3, but is considerably smaller than that of H_2NMg^+–NH_3.

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