Available online at www.sciencedirect.com
ScienceDirect
International Journal of Mass Spectrometry 255–256 (2006) 11–19
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Ligation of Be^+ and Mg^+ to NF_3: Structure, stability, and thermochemistry of the Be^+–(NF_3) and Mg^+–(NF_3) complexes

Stefano Borocci, Nicoletta Bronzolino, Maria Giordani, Felice Grandinetti [*]

Dipartimento di Scienze Ambientali, Università della Tuscia, Largo dell' Università, 01100 Viterbo, Italy

Received 1 June 2005; accepted 21 July 2005
Available online 6 September 2005

Dedicated to Professor Diethard K. Bohme on the occasion of his 65th birthday.

Abstract

The structure, stability, and thermochemistry of the still experimentally unknown Be^+–(NF_3) and Mg^+–(NF_3) complexes have been theoretically investigated at the B3LYP, RCCSD, and RCCSD(T) levels of theory in conjunction with the 6-311G(d), 6-311 + G(2d), and 6-311 + G(3df) basis sets. Compared with the previously investigated H^+–(NF_3), Li^+–(NF_3), Na^+–(NF_3), and K^+–(NF_3), the study of M^+–(NF_3) (M = Be or Mg) has revealed novel and somewhat unexpected features of the interaction of NF_3 with monoatomic ions. Thus, irrespective of the employed theoretical level, the ligation of Be^+ and Mg^+ to NF_3 leads to the formation of two distinct isomers, namely the M^+–NF_3 nitrogen-coordinated complexes **1** (M = Be) and **5** (M = Mg) and the insertion products of F_2N–MF^+ connectivity **2** (M = Be) and **6** (M = Mg). On the other hand, at variance with M^+–(NF_3) (M = Li, Na, and K), neither the fluorine-monocoordinated nor the fluorine-dicoordinated structure were located as minima on the potential energy surface. The geometry and bonding analysis of the M^+–NF_3 isomers **1** and **5** and of the F_2N–MF^+ isomers **2** and **6** point to ion–dipole complexes between M^+ and NF_3 and MF^+ and NF_2, respectively. At the RCCSD(T)/6-311 + G(2d)//RCCSD/6-311G(d) level of theory and 298.15 K, the insertion products **2** and **6** are more stable than the nitrogen-coordinated isomers **1** and **5** by 109.2 and 59.2 kcal mol^{-1}, respectively. In addition, assuming the formation of **2** and **6**, the Be^+ and Mg^+ ion affinities of NF_3 result as high as 127.3 and 62.5 kcal mol^{-1}, respectively. Our results suggest that the Be^+–(NF_3) and Mg^+–(NF_3) complexes could be actually observed as stable species in the gas phase, and support the proposal that techniques such as Mg^+ ion attachment mass spectrometry could be used to quantify the emissions of NF_3, one of the perfluorocompounds most extensively used in semiconductor technology.

Keywords: Ab initio; Beryllium cation; DFT; Magnesium cation; Nitrogen trifluoride

1. Introduction

The structure and stability of the complexes of nitrogen trifluoride, NF_3, with monoatomic and simple polyatomic ions have been investigated by various experimental and theoretical methods [1–7]. From the fundamental point of view, these studies have provided detailed information on the behavior of NF_3 as a bifunctional Lewis base. In addition, they serve to evaluate the possibility of using techniques such as Li^+-attachment mass spectrometry [8–10] to quantify the industrial emissions of NF_3, which is one of the gaseous perfluorocompounds most extensively used in the electronic industry to perform etching and cleaning processes [11,12].

In the gaseous phase, the thermodynamically favoured protonation site of nitrogen trifluoride is the fluorine atom, the nitrogen atom being less basic by ca. 6–8 kcal mol^{-1} [1–4]. On the other hand, the experimental and theoretical studies on the adducts of $NF_2{}^+$ [3,6] and $CH_3{}^+$ [4] with NF_3 indicated that these two ions add preferentially to the nitrogen atom, the ligation to fluorine being unfavoured by ca. 9 kcal mol^{-1} for $NF_2{}^+$ and ca. 23 kcal mol^{-1} for $CH_3{}^+$. Our investigation of the Li^+–(NF_3) complexes [5] confirmed that, similarly to H^+, the ligation of the monoatomic ion Li^+ occurs preferentially at the fluorine atoms of NF_3, with formation of monocoordinated and dicoordinated isomers which

---

[*] Corresponding author. Tel.: +39 0761 357 116; fax: +39 0761 357 179.
E-mail address: fgrandi@unitus.it (F. Grandinetti).

1387-3806/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2005.07.009

are practically degenerate and more stable than the nitrogen-coordinated isomer by ca. 5 kcal mol^{-1} at the CCSD(T)/6-311 + G(2d)//B3LYP/6-311 + G(2d) level of theory. In addition, at the same computational level, the Li^+ ion affinity of NF_3 at 298.15 K resulted as ca. 13 kcal mol^{-1}. Our theoretical results have been quite recently confirmed by Li and co-workers [7], who have also found that, at the QCISD/6-311 + G(2d) level of theory, the most stable isomer of all the M^+–(NF_3) complexes (M = Li, Na, and K) is the fluorine-dicoordinated structure, which is practically degenerate with the fluorine-monocoordinated structure and is more stable than the nitrogen-coordinated isomer by ca. 4 kcal mol^{-1} for M = Li and ca. 3 kcal mol^{-1} for M = Na and K. In addition, Li and co-workers [7] have found that, passing from Li^+ to K^+, the gas-phase cation affinity of NF_3 sharply decreases from ca. 13 to ca. 7 kcal mol^{-1}, and becomes even smaller, ca. 5 kcal mol^{-1}, for K^+. Stimulated by these previous studies on the interaction of monoatomic ions M^+ with NF_3, as part of our continuing experimental and theoretical interest in the gas-phase chemistry of this molecule [2,4–6,13–21], we decided to extend the investigation to the adducts of NF_3 with the second-group monoatomic ions Be^+ and Mg^+. The study of Be^+–(NF_3) and Mg^+–(NF_3) is of interest for several reasons. First, NF_3 is a prototype ligand to probe still unexplored features of the Lewis acidity of Be^+ and Mg^+. Thus, despite the intensive experimental and theoretical interest focused over the years on the complexes of the beryllium and magnesium monocations with a variety of inorganic and organic ligands, clearly summarized in various recent studies [22–41] and in exhaustive review articles [42,43], the ligation of Be^+ and Mg^+ to fluorinated molecules is still essentially unexplored. Second, the study of the interaction of NF_3 with open-shell cations such as Be^+ and Mg^+ could provide novel information on the behavior of this molecule as a bifunctional Lewis base. Third, the magnesium-cation affinity of nitrogen trifluoride could be large enough to suggest the possible use of Mg^+ ion mass spectrometry to detect gaseous NF_3. As a matter of fact, the theoretical results discussed in the present article outline a strong affinity of both Be^+ and Mg^+ for the fluorine atoms of NF_3, and the detailed investigation of the structure, stability, and thermochemistry of the Be^+–(NF_3) and Mg^+–(NF_3) complexes not only confirms their conceivable formation as stable gaseous species but also reveals novel and somewhat unexpected features of the interaction of NF_3 with monoatomic ions M^+.

2. Computational details

All the calculations have been performed with the GAUSSIAN 98 [44] and MOLPRO 2000.1 [45] sets of programs. Using the standard internal 6-311G(d), 6-311 + G(2d), and 6-311 + G(3df) basis sets [46–49], the geometries were first optimized at the Becke's three-parameter hybrid functional level of theory, B3LYP [50], where the non-local correlation is provided by the Lee–Yang–Parr expression [51], and subsequently refined, with the 6-311G(d) basis set, at the restricted Coupled Cluster level of theory [52–55], including the contribution from single and double substitutions. The RCCSD/6-311G(d) optimized geometries were also used to perform single-point calculations, with the 6-311G(d) and the 6-311 + G(2d) basis sets, at the restricted Coupled Cluster level of theory, so to include the contribution of connected triple excitations, RCCSD(T). The obtained structures were ascertained to be true minima or higher order saddle points on the B3LYP potential energy surface by calculating their harmonic vibrational frequencies, whose unscaled values were also used to evaluate the zero-point energies and the vibrational contribution to the thermal correction at 298.15 K [56] (both the translational and the rotational contribution have been evaluated as 3/2RT). The basis set superposition error (BSSE) has been estimated according to the method by Boys and Bernardi [57]. Chemical bonding analysis was based on the theory of Atoms-in-Molecules [58], using the implementation in GAUSSIAN 98 due to Cioslowski and co-workers [59,60] and the AIM2000 program package [61]. In particular, we have calculated the B3LYP/6-311 + G(2d) total charges q, the charge density ρ and the Laplacian of the charge density $\nabla^2\rho$ at the bond critical points (bcp), intended as the points on the attractor interaction lines where $\nabla\rho = 0$, and the covalent bond order of the various chemical bonds.

3. Results and discussion

3.1. Structure and stability of the Be^+–(NF_3) and Mg^+–(NF_3) complexes

The connectivities of the various Be^+–(NF_3) and Mg^+–(NF_3) isomers presently located as stationary points on the B3LYP and RCCSD potential energy surfaces, henceforth indicated as **1**–**4** and **5**–**8**, respectively, are shown in Figs. 1 and 2. Their detailed geometries and chemical bonding analysis are collected in Tables 1–3, and their relative energies at 0 and 298.15 K are reported in Table 4.

For comparative purposes and also to appreciate the performance of the various employed theoretical levels, we have also investigated the uncoordinated NF_3. Thus, we first note that all the employed theoretical levels correctly predict the experimental F–N–F bond angle of NF_3, 102.2° [62]. On the other hand, the calculated N–F bond length is more sensitive to the theoretical level and to the size of the basis set, and spans from 1.361 Å at the RCCSD/6-311G(d) to 1.382 Å at the B3LYP/6-311 + G(2d) level. It is however of interest to note the good agreement between the B3LYP/6-311 + G(3df) value of 1.375 Å and the experimental value of 1.371 Å [62].

The addition of doublet ground state Be^+ ($1s^22s\ ^2S$) [63] to the nitrogen atom of NF_3 leads to the formation of the C_{3v}-symmetry ion **1**, which was characterized, with any basis set, as a true minimum on the B3LYP potential energy surface. Irrespective of the employed computational level and basis set, the Be–N distance of this ion is invariably pre-

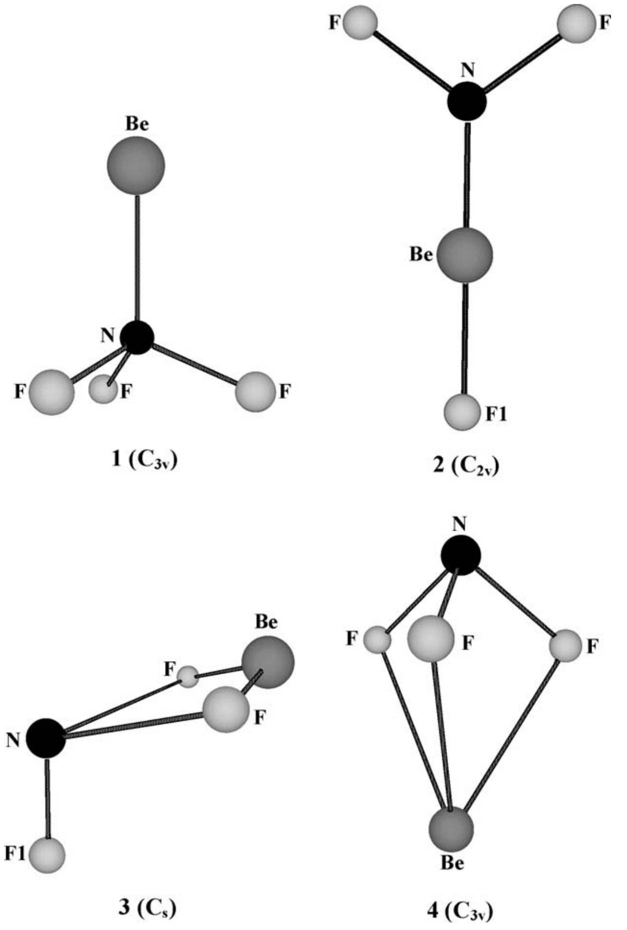

Fig. 1. Connectivities of the Be^+–(NF_3) ions **1**–**4**.

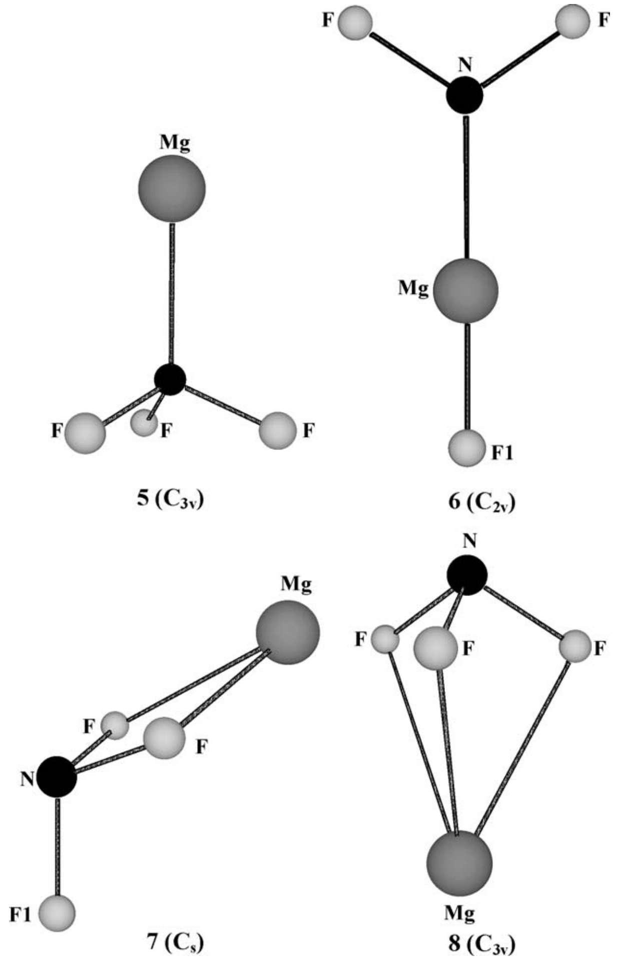

Fig. 2. Connectivities of the Mg^+–(NF_3) ions **5**–**8**.

dicted to be larger than 1.8 Å and is structurally telling of an ion–dipole complex between Be^+ and NF_3. From Table 3, the charge at the Be atom is +0.981e and the Be–N covalent bond order is less than 0.3. In addition, at the bond critical point on the attractor interaction line corresponding to the Be–N bond, the charge density ρ is as small as 0.379 e/Å^3 and the Laplacian of ρ is positive, which is typical of non-covalent bonding interactions. From Table 1, as already noted for the F–N–F bond angle of NF_3, the Be–N–F and F–N–F bond angles of **1** are practically independent on the employed level of theory and on the size of the basis set and range around 113.0° and 106.0°, respectively. In addition, the optimized parameters and bonding analysis of **1** reveal that the formal attachment of Be^+ to the N atom of NF_3 promotes a charge shift from the surrounding fluorines and enhances the degree of N–F interaction. Thus, irrespective of the basis set employed at the B3LYP level and also at the RCCSD/6-311G(d) level of theory, the N–F distance of **1** is shorter than uncoordinated NF_3 by ca. 0.03 Å, and the F–N–F bond angle is larger by ca. 4°. Isomer **1** is the corresponding analogue of the nitrogen-coordinated complex between Be^+ and NH_3, recently located as a minimum of C_{3v} symmetry on the MP2(full)/6-311 ++ G(d,p) potential energy surface [37]. Compared with NF_3, the interaction of Be^+ with the N atom of NH_3 is stronger (*vide infra*), and, consistently, the Be–N distance of Be^+–NH_3 has been predicted as 1.683 Å [37].

Compared with the previously investigated H^+–(NF_3) [1–4], Li^+–(NF_3) [5,7], Na^+–(NF_3) [7], and K^+–(NF_3) [7], the study of the ligation of doublet Be^+ to the fluorine atoms of NF_3 lead to somewhat unexpected results. Thus, in line with the well ascertained ability of NF_3 to form stable fluorine-monocoordinated adducts of F_2N–F–X^+ connectivity (X = H, Li, Na, and K), we first tried to locate a conceivably stable F_2N–F–Be^+ isomer. However, despite careful searching at various levels of theory, we did not find any critical point with this connectivity. Rather, the approach of Be^+ to one of the fluorine atoms of NF_3 invariably resulted in a significant elongation of the N–F bond, in the concomitant rotation of the ensuing BeF^+, and in the eventual formation of the "insertion" product **2** of F_2N–Be–F^+ connectivity. As a matter of fact, the geometry, bonding analysis, and thermochemistry of this isomer suggest a tightly bound ion–dipole complex between ground state BeF^+ ($^1\Sigma^+$) [64] and NF_2 ($^2B_1$) [65]. From Table 3, the net charge of the BeF^+ moiety is almost +1e, the Be–N covalent bond order is less than 0.2, the charge density ρ at the bcp on the attractor interaction line corresponding to the Be–N bond is as small as 0.512 e/Å^3, and

Table 1
Optimized geometries of the Be^+–(NF_3) complexes **1**–**4** and NF_3

Parameter	B3LYP			RCCSD
	6-311G(d)	6-311 + G(2d)	6-311 + G(3df)	6-311G(d)
1 ($^2A_1$)				
Be—N	1.843	1.844	1.840	1.840
N—F	1.346	1.348	1.342	1.333
Be—N—F	112.6	112.8	112.8	112.6
F—N—F	106.2	105.9	106.0	106.2
2 ($^2B_1$)				
Be—N	1.698	1.699	1.702	1.707
Be—F1	1.335	1.331	1.330	1.336
N—F	1.297	1.299	1.295	1.290
Be—N—F	124.7	124.8	124.9	124.7
3 ($^2A'$)				
Be—N	2.440	2.452	2.438	2.733
Be—F	1.407	1.399	1.396	1.393
N—F	2.317	2.332	2.324	2.601
N—F1	1.212	1.213	1.207	1.181
F—Be—F	135.8	136.5	136.7	139.3
F—N—F	68.5	67.7	67.9	60.3
F—N—F1	115.0	114.8	114.6	100.4
3 ($^2A''$)				
Be—N	2.509	2.509	2.502	2.685
Be—F	1.407	1.398	1.397	1.395
N—F	2.294	2.303	2.299	2.493
N—F1	1.213	1.214	1.208	1.185
F—Be—F	128.9	129.7	129.9	133.8
F—N—F	67.2	66.7	66.8	62.0
F—N—F1	102.7	102.8	102.8	100.1
4 ($^2A_1$)				
Be—F	2.383	2.363	2.295	2.356
N—F	1.394	1.395	1.390	1.376
Be—F—N	87.3	87.0	86.3	87.3
F—N—F	99.3	99.3	99.2	99.4
NF_3 ($^1A_1$)				
N—F	1.380	1.382	1.375	1.361
F—N—F	102.1	101.9	102.0	102.2

Bond lengths in angstroms, bond angles in degrees (for connectivities and labeling of the atoms, see Fig. 1).

Table 2
Optimized geometries of the Mg^+–(NF_3) complexes **5**–**8**

Parameter	B3LYP			RCCSD
	6-311G(d)	6-311 + G(2d)	6-311 + G(3df)	6-311G(d)
5 ($^2A_1$)				
Mg—N	2.517	2.538	2.519	2.528
N—F	1.359	1.362	1.356	1.345
Mg—N—F	114.1	114.4	114.3	114.1
F—N—F	104.4	104.1	104.3	104.4
6 ($^2B_1$)				
Mg—N	2.195	2.179	2.180	2.208
Mg—F1	1.734	1.720	1.712	1.733
N—F	1.311	1.313	1.308	1.302
Mg—N—F	125.7	125.8	125.9	125.8
7 ($^2A'$)				
Mg—N	3.147	3.175	3.133	3.189
Mg—F	2.454	2.487	2.451	2.508
N—F	1.440	1.437	1.430	1.402
N—F1	1.315	1.322	1.316	1.319
F—Mg—F	52.3	51.6	52.2	50.0
F—N—F	97.4	97.8	97.9	98.3
F—N—F1	102.7	102.5	102.6	102.6
8 ($^2A_1$)				
Mg—F	2.872	2.928	2.889	2.916
N—F	1.388	1.390	1.383	1.370
Mg—F—N	91.9	92.4	92.0	92.5
F—N—F	100.6	100.6	100.7	100.7

Bond lengths in angstroms, bond angles in degrees (for connectivities and labeling of the atoms, see Fig. 2).

the corresponding Laplacian is definitely positive. In addition, at the RCCSD/6-311G(d) Be–N distance of 1.707 Å, the dissociation enthalpy at 298.15 K of **2** into BeF^+ and NF_2 is computed as 42.3 kcal mol^{-1} at the RCCSD(T)/6-311 + G(2d)//RCCSD/6-311G(d) level of theory (including a BSSE correction of 3.9 kcal mol^{-1}). However, the probably most relevant finding concerning isomer **2** is its exceedingly larger stability with respect to **1**. Thus, from Table 4, at any computational level, the enthalpy difference between the two isomers results as ca. 110 kcal mol^{-1}, and is predicted in particular as 109.2 kcal mol^{-1} at the highest RCCSD(T)/6-311 + G(2d)//RCCSD/6-311G(d) level of theory. Compared with the previously investigated M^+–(NF_3) isomeric structures (M = H, Li, Na, and K) [1–5,7], whose nitrogen- and fluorine-coordinated isomers are usually quite close in energy (*vide infra*), the relative stability of the Be^+–(NF_3) isomers **1** and **2** is somewhat unexpected and provides the first case of by far stability of the fluorine-coordinated isomer from the ligation of NF_3 to a singly charged gaseous cation.

At the B3LYP level of theory, with any employed basis set, the dicoordinated ion **3** of C_s symmetry is a first-order saddle point, unstable with respect to the formation of two equivalent isomers **2**. The two electronic states $^2A'$ and $^2A''$ of this ion (the B3LYP/6-311 + G(3df) imaginary frequencies are 755.1i ($^2A'$) and 462.5i cm^{-1} ($^2A''$), respectively), are practically degenerate and less stable than isomer **2** by ca. 10 kcal mol^{-1}. Their optimized geometries and bonding analysis are consistently quite similar and point to weakly bound electrostatic complexes between ground state NF^+ ($^2\Pi$) [66] and BeF_2 ($^1\Sigma_g{}^+$) [67]. In particular, at the RCCSD(T)/6-311 + G(2d)//RCCSD/6-311G(d) level of theory and 298.15 K, they are more stable than the separated NF^+ and BeF_2 by only 3.1 ($^2A'$) and 4.2 kcal mol^{-1} ($^2A''$), respectively. Finally, the tricoordinated structure **4** is the least stable of all the fluorine-coordinated Be^+–(NF_3) ions, and is also less stable that the nitrogen-coordinated structure **1** by ca. 9 kcal mol^{-1}. It is in fact a second-order saddle point on the B3LYP potential energy surface, unstable with respect to the degenerate bending motion of the beryllium atom (the B3LYP/6-311 + G(3df) doubly degenerate imaginary frequency is 209.6i cm^{-1}).

The results on the complexes between doublet ground state Mg^+ ([Ne]3s ^2S) and NF_3 are qualitatively similar to those obtained for the Be^+–(NF_3) complexes. In fact, on the B3LYP potential energy surface, with any basis set, we have located the nitrogen-coordinated isomer **5** and the insertion product **6** of F_2N–Mg–F^+ connectivity as energy minima [68], the dicoordinated ion **7** as a first-order saddle

Table 3
B3LYP/6-311 + G(2d) Atoms-in-Molecules (AIM) analysis of $\mathrm{NF_3}$, of the $\mathrm{Be^+}$–($\mathrm{NF_3}$) complexes **1**–**4**, and of the $\mathrm{Mg^+}$–($\mathrm{NF_3}$) complexes **5**–**8** (see Figs. 1 and 2)

Species	q (Be or Mg)[a]	q (N)[a]	q (F)[a]	q (F1)[a]	Bond	ρ[b]	$\nabla^2\rho$[c]	BO[d]
$\mathrm{NF_3}$ ($^1\mathrm{A}_1$)		0.732	−0.244		N—F	2.058	−2.747	1.208
1 ($^2\mathrm{A}_1$)	0.981	0.570	−0.182		Be—N	0.379	5.446	0.283
					N—F	2.348	−7.061	1.212
2 ($^2\mathrm{B}_1$)	1.751	0.359	−0.145	−0.821	Be—N	0.512	8.362	0.162
					Be—F1	1.140	38.462	0.358
					N—F	2.585	−13.592	1.407
3 ($^2\mathrm{A}'$)	1.763	0.827	−0.763	−0.063	Be—F	0.911	28.798	0.260
					N—F	0.209	3.085	0.304
					N—F1	3.165	−32.534	1.753
3 ($^2\mathrm{A}''$)	1.768	0.827	−0.765	−0.070	Be—F	0.911	28.916	0.256
					N—F	0.213	2.844	0.292
					N—F1	3.151	−32.196	1.736
4 ($^2\mathrm{A}_1$)	0.988	0.887	−0.300		Be—F	0.108	0.105	0.112[e]
					N—F	2.045	−3.085	1.125[e]
5 ($^2\mathrm{A}_1$)	0.991	0.702	−0.226		Mg—N	0.123	1.229	0.193
					N—F	2.247	−5.880	1.182
6 ($^2\mathrm{B}_1$)	1.769	0.428	−0.180	−0.834	Mg—N	0.229	4.531	0.138
					Mg—F1	0.597	20.773	0.391
					N—F	2.477	−11.688	1.379
7 ($^2\mathrm{A}'$)	1.022	0.873	−0.359	−0.186	Mg—F	0.094	1.104	0.003
					N—F	1.822	0.581	1.072
					N—F1	2.490	−10.965	1.257
8 ($^2\mathrm{A}_1$)	1.010	0.878	−0.300		Mg—F	0.050	0.282	0.071
					N—F	2.072	−3.470	1.127

[a] AIM formal charge (e).

[b] Charge density (e/Å^3) at the bond critical point on the specified bond.

[c] Laplacian of the charge density (e/Å^5) at the bond critical point on the specified bond.

[d] Covalent bond order of the specified bond.

[e] At the B3LYP/6-311 + G(d) level of theory.

point, and the tricoordinated ion **8** as a second-order saddle point. However, from the quantitative point of view, the $\mathrm{Be^+}$–($\mathrm{NF_3}$) and $\mathrm{Mg^+}$–($\mathrm{NF_3}$) ions feature significant differences, which arise essentially from the weaker Lewis acidity of $\mathrm{Mg^+}$ and $\mathrm{MgF^+}$ with respect to $\mathrm{Be^+}$ and $\mathrm{BeF^+}$. Similarly to the corresponding $\mathrm{Be^+}$–$\mathrm{NF_3}$ isomer **1**, the bonding analysis of isomer **5** points to an electrostatic complex between $\mathrm{Mg^+}$ and $\mathrm{NF_3}$. Compared with the addition of $\mathrm{Be^+}$ to the N atom of $\mathrm{NF_3}$, which is exothermic by ca. 18 kcal mol^{-1} at the RCCSD(T)/6-311 + G(2d)//RCCSD/6-311G(d) level of theory, the corresponding interaction of $\mathrm{Mg^+}$ is much weaker and amounts to ca. 3 kcal mol^{-1}. Consistently, from Table 2, the Mg–N distance of **5** is as long as ca. 2.5 Å, and the structural parameters, charge distribution, and charge density of the $\mathrm{NF_3}$ moiety are only slightly different from the uncoordinated $\mathrm{NF_3}$.

Similarly to isomer **2**, the insertion product **6** is an ion–dipole complex between ground state $\mathrm{NF_2}$ and $\mathrm{MgF^+}$

Table 4
Relative stabilities (kcal mol^{-1}) at 0 K (in parentheses) and 298.15 K of the $\mathrm{Be^+}$–($\mathrm{NF_3}$) complexes **1**–**4** and the $\mathrm{Mg^+}$–($\mathrm{NF_3}$) complexes **5**–**8**

Species	B3LYP			RCCSD(T)[a]	
	6-311G(d)	6-311 + G(2d)	6-311 + G(3df)	6-311G(d)	6-311 + G(2d)
1 ($^2\mathrm{A}_1$)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
2 ($^2\mathrm{B}_1$)	−110.8 (−111.2)	−111.3 (−111.7)	−110.4 (−110.9)	−108.5 (−109.0)	−109.2 (−109.7)
3 ($^2\mathrm{A}'$)	−98.4 (−98.7)	−99.8 (−100.1)	−97.9 (−98.3)	−97.2 (−97.6)	−100.2 (−100.6)
3 ($^2\mathrm{A}''$)	−100.1 (−100.4)	−101.6 (−101.9)	−99.8 (−100.1)	−98.3 (−98.6)	−101.3 (−101.6)
4 ($^2\mathrm{A}_1$)	+9.0 (+9.5)	+10.2 (+10.7)	+10.3 (+10.8)	+9.1 (+9.6)	+8.8 (+9.3)
5 ($^2\mathrm{A}_1$)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
6 ($^2\mathrm{B}_1$)	−54.9 (−55.4)	−57.2 (−57.7)	−57.7 (−58.3)	−56.0 (−56.6)	−59.2 (−59.8)
7 ($^2\mathrm{A}'$)	−4.8 (−4.4)	−2.6 (−2.2)	−2.5 (−2.2)	−4.2 (−3.9)	−3.0 (−2.7)
8 ($^2\mathrm{A}_1$)	−2.6 (−1.7)	−0.5 (+0.4)	−0.4 (+0.5)	−2.7 (−1.8)	−1.6 (−0.7)

[a] At the RCCSD/6-311G(d) optimized geometries.

($^1\Sigma^+$) [69]. The net charge of the MgF^+ moiety is almost +1e, the Mg–N covalent bond order is less than 0.2, the charge density ρ at the bcp on the attractor interaction line corresponding to the Mg–N bond is as small as 0.229 e/Å^3 and the corresponding Laplacian is positive. In addition, from Table 2, the Mg–N bond distance, computed as ca. 2.2 Å, is appreciably longer than the Be–N distance of isomer **2**, and the dissociation enthalpy into MgF^+ and NF_2, computed as 17.9 kcal mol^{-1} at the RCCSD(T)/6-311 + G(2d)//RCCSD/6-311G(d) level of theory and 298.15 K (including a BSSE correction of 1.8 kcal mol^{-1}), is consistently lower than the dissociation enthalpy of **2** into BeF^+ and NF_2. From Table 4, at the RCCSD(T)/6-311 + G(2d)//RCCSD/6-311G(d) level of theory and 298.15 K, isomer **6** is more stable than **5** by 59.2 kcal mol^{-1}. Although this difference is significantly lower than the enthalpy gap between the Be^+–(NF_3) isomers **1** and **2**, it still clearly indicates that, similarly to Be^+, the product of the insertion of Mg^+ into the N–F bond of NF_3 is by far more stable than the nitrogen-coordinated adduct. In this respect, it is of interest to note that, as part of a detailed theoretical investigation on the structure and stability of the Mg^+–(NH_3) complexes [23], Bohme and co-workers have located the insertion product H_2N–Mg–H^+ as a minimum on the B3LYP/6-31 + G(d) potential energy surface. However, at this level of theory, this species resulted less stable than the nitrogen-coordinated isomer by 51.0 kcal mol^{-1} and even higher in energy than the isolated Mg^+ and NH_3 by 10.7 kcal mol^{-1}. These findings clearly evidence the profound effect of the degree of fluorination on the relative stability of the Mg^+–NX_3 and X_2N–MgX^+ isomeric structures (X = H and F).

The relatively lower affinity of Mg^+, compared with Be^+, for the fluorine atoms of NF_3 is clearly evident from the optimized geometry of the dicoordinated structure **7**, which is the transition structure for the interconversion of two equivalent isomers **6** (the B3LYP/6-311 + G(3df) imaginary frequency is 96.3i cm^{-1}). At variance with the corresponding ion **3**, which is a complex between NF^+ and BeF_2 (the charge at the Be atom is ca. +1.8e), ion **7** is a complex between Mg^+ and NF_3. From Fig. 2 and Table 2, the charge at the Mg atom is ca. +1.0e, the Mg–F bond distances are as long as ca. 2.5 Å, and the parameters of the NF_3 moiety show only minor deviations from uncoordinated NF_3. The interaction between Mg^+ and NF_3, clearly electrostatic from the results of the bonding analysis, amounts to 5.7 kcal mol^{-1} at the RCCSD(T)/6-311 + G(2d)//RCCSD/6-311G(d) level of theory and 298.15 K. Therefore, ion **7** is slightly more stable than the nitrogen-coordinated isomer **5**, but is less stable than the insertion product **6** by ca. 55 kcal mol^{-1}. The characterization of **7** as a first-order saddle point is in line with the results of a very recent study by Dunbar and Petrie [41] on the complexes of the magnesium monocation with a variety of ligands, including difunctional molecules such as HCOOH, CH_3COOH, $HCOOCH_3$, $HCOCH_2OH$, and $HCONH_2$. In particular, only $HCOCH_2OH$ was found to form a truly bidentate complex with Mg^+, whereas all efforts to locate chelating geometries with HCOOH, CH_3COOH, and $HCOOCH_3$ invariably resulted in the collapse to one or other of the monodentate complexes between Mg^+ and the carbonyl or the sp^3 O atom.

Similarly to ion **4**, the tricoordinated structure **8** is unstable with respect to the degenerate bending motion of the magnesium atom (the B3LYP/6-311 + G(3df) doubly degenerate imaginary frequency is 83.0i cm^{-1}). The electrostatic interaction between Mg^+ and NF_3 is even weaker than ion **7** and amounts to 4.3 kcal mol^{-1} at the RCCSD(T)/6-311 + G(2d)//RCCSD/6-311G(d) level of theory.

3.2. Be^+ and Mg^+ ion affinity of NF_3: thermochemistry of the Be^+–(NF_3) and Mg^+–(NF_3) complexes

The gas-phase beryllium and magnesium cation affinity of NF_3, defined here as the minus enthalpy change of the reaction

$$M^+ + NF_3 \rightarrow M^+\text{–}(NF_3) \quad (M = \text{Be or Mg}) \tag{1}$$

obtained at various computational levels assuming the formation of the nitrogen-coordinated isomers **1** and **5** and of the insertion products **2** and **6** are collected in Table 5. We have also calculated the Be^+ and Mg^+ ion affinity of NH_3 and compared our results with previous experimental and theoretical studies on Be^+–NH_3 [37] and Mg^+–NH_3 [23,27,28,41,70].

Generally speaking, we first note that at both the B3LYP and the RCCSD(T) level of theory, the smallest 6-311G(d) basis set slightly overestimates the experimental Mg^+ ion affinity of ammonia, obtained by collision-induced dissociation measurements [27] as 36.9 ± 2.8 kcal mol^{-1} at 0 K and extrapolated as 38.0 ± 2.8 kcal mol^{-1} at 298 K. On the other hand, all the values calculated at 0 K using the larger 6-311 + G(2d) and 6-311 + G(3df) basis sets range around 37 kcal mol^{-1}, and the RCCSD(T)/6-311 + G(2d)//RCCSD/6-311G(d) estimate of 36.9 kcal mol^{-1} (corrected to 38.0 kcal mol^{-1} at 298.15 K) coincides with the experimental value. Passing to NF_3, the scarce experience on the calculation of the Be^+ and Mg^+ ion affinities of simple fluorinated molecules prevents a critical evaluation of the B3LYP and RCCSD(T) estimates reported in Table 5. We note however that all the obtained values show largest deviations of less than 2 kcal mol^{-1}, and we will refer here to the in principle most accurate data obtained at the RCCSD(T)/6-311 + G(2d)//RCCSD/6-311G(d) level of theory.

At 298.15 K, the ligation of Be^+ to the N atom of NF_3, with formation of isomer **1**, is exothermic by 18.1 kcal mol^{-1}. This value is much lower than the Be^+ ion affinity of NH_3, previously estimated as 75.2 kcal mol^{-1} [37] and presently obtained as 75.9 kcal mol^{-1}, and confirms the sharp decrease of basicity of the nitrogen atom usually found with any electrophile passing from NH_3 to NF_3. However, if one considers the formation of the insertion product **2**, the

Table 5
Be^+ (upper values) and Mg^+ ion affinities (kcal mol^{-1}) at 0 K (in parentheses) and 298.15 K of NH_3 and NF_3 (all the presently obtained values include the BSSE)

	B3LYP			RCCSD(T)[a]		Literature	
	6-311G(d)	6-311 + G(2d)	6-311 + G(3df)	6-311G(d)	6-311 + G(2d)	Experiment	Theory
NH_3	75.8 (74.6)	75.2 (73.9)	75.5 (74.2)	78.9 (77.6)	75.9 (74.6)		75.2[b]
	40.5 (39.4)	38.4 (37.2)	38.3 (37.2)	39.6 (38.5)	38.0 (36.9)	36.9 ± 2.8[c]	35.5[d]; 36.1[e]; 37.7[f]; 38.3[b]; 39.7[g]; 40.1[h]; 40.5[i]
NF_3(N)[j]	20.3 (19.7)	20.3 (19.7)	21.3 (20.7)	18.1 (17.5)	18.1 (17.5)		
	4.7 (4.6)	4.5 (4.3)	5.1 (5.0)	3.2 (3.1)	3.3 (3.2)		
NF_3(F)[k]	131.1 (130.9)	131.6 (131.4)	131.7 (131.6)	126.6 (126.5)	127.3 (127.2)		
	59.6 (60.0)	61.7 (62.0)	62.8 (63.3)	59.2 (59.7)	62.5 (63.0)		

[a] At the RCCSD/6-311G(d) optimized geometries.

[b] At the CCSD(T)(full)/6-311 ++ G(d,p)//MP2(full)/6-311 ++ G(d,p) level of theory, Ref. [37].

[c] Collision-induced dissociation measurement at 0 K, Ref. [27]. The 298 K-extrapolated value given in the same paper is 38.0 ± 2.8 kcal mol^{-1}.

[d] At the MP2(full)/6-311 + G(2d,2p)//MP2(full)/6-31G(d) level of theory and 0 K, Ref. [27].

[e] At the CP-dG2thaw level of theory, Ref. [41].

[f] At the MCPF/TZP level of theory and 0 K, Ref. [70].

[g] At the MP4SDTQ(fc)/6-311 ++ G(2df,p) level of theory, Ref. [23].

[h] At the B3LYP/DZVP level of theory, Ref. [28].

[i] At the B3LYP/6-31 + G(d) level of theory, Ref. [28].

[j] With formation of isomers **1** and **5**, respectively.

[k] With formation of isomers **2** and **6**, respectively.

enthalpy change of reaction (1) (M = Be) becomes as large as −127.3 kcal mol^{-1}, and the Be^+ ion affinity of NF_3 results higher than NH_3 by more than 50 kcal mol^{-1}. This somewhat surprising result simply reflects the high stability of isomer **2** and clearly suggests that, with selected electrophiles, NF_3 may behave as a strong Lewis base, able to form “insertion” products of exceptional thermodynamic stability. This conclusion is confirmed by the thermochemistry of the complexation of NF_3 by Mg^+. Thus, if one considers the ligation to the N atom, the Mg^+ ion affinity of NF_3, 3.3 kcal mol^{-1}, is even lower than poor ligands such as CO and CO_2 [41]. However, if one assumes the formation of the insertion product **6**, the enthalpy change of reaction (1) (M = Mg) becomes as large as −62.5 kcal mol^{-1}, and the Mg^+ ion affinity of NF_3 becomes significantly higher than NH_3 and other strong ligands such as H_2NCN and $HCONH_2$, whose Mg^+ affinities range around 45 and 48 kcal mol^{-1}, respectively [41]. We note also that the Be^+ and Mg^+ ion affinities of NF_3 are large enough to suggest their conceivable observation as stable species in the gas phase. This supports the proposal that Mg^+ ion attachment mass spectrometry could be used as a conceivable technique to detect gaseous nitrogen trifluoride.

Combining the enthalpy changes at 298.15 K of reaction (1) (M = Be or Mg) with the experimental enthalpy of formation of Be^+, 292.4 kcal mol^{-1}; Mg^+, 211.5 kcal mol^{-1}; NF_3, −31.6 kcal mol^{-1}, the enthalpies of formation of isomers **1** and **5** are obtained as 242.7 and 176.6 kcal mol^{-1}, respectively. Using the relative stabilities reported in Table 4, the enthalpies of formation of the various Be^+–(NF_3) and Mg^+–(NF_3) ions are obtained as 133.5 (**2**), 142.5 (**3**($^2A'$)), 141.4 (**3**($^2A''$)), 251.5 (**4**), 117.4 (**6**), 173.6 (**7**), and 175.0 (**8**) kcal mol^{-1}, respectively.

3.3. Comparison between the various M^+–(NF_3) complexes (M = H, Li, Na, K, Be, and Mg)

The comparison between the presently investigated Be^+–(NF_3) and Mg^+–(NF_3) and the previously investigated M^+–(NF_3) (M = H, Li, Na, and K) [1–5,7] suggests general considerations on the factors which control the structure and stability of the complexes of NF_3 with monoatomic ions M^+.

Due to the electron withdrawing effect of the three fluorine atoms, the nitrogen atom of NF_3 is usually much less basic than NH_3. Thus, compared with the proton affinity of NH_3, 204.0 kcal mol^{-1}, the addition of H^+ to NF_3 with formation of $H–NF_3^+$ is exothermic by ca. 130 kcal mol^{-1} [1–4], and the absolute affinities of Li^+, Na^+, and K^+ for the N atom of NF_3, evaluated as 7.5, 3.4, and 2.0 kcal mol^{-1}, respectively [7], are appreciably lower than the Li^+, Na^+, and K^+ affinities of NH_3, which amount to 39.1 [71], 24.4 [72], and 19.6 kcal mol^{-1} [73], respectively. Consistently, our calculated Be^+ and Mg^+ affinities for the N atom of NF_3 are significantly lower than NH_3. In addition, all the N-coordinated $M^+–NF_3$ complexes (M = Li, Na, K, Be, and Mg) are invariably predicted to be electrostatic, and their orders of stability follow similar periodic trends, namely $Li^+ < Na^+ < K^+$, and $Be^+ < Mg^+$. Concerning the ligation of M^+ to the F atom(s) of NF_3, the present characterization of the “insertion” products $F_2N–BeF^+$ and $F_2N–MgF^+$ as ion–molecule complexes between NF_2 and MF^+ (M = Be and Mg), the previous identification of the $F_2N–FH^+$ isomer as an electrostatic complex between NF_2^+ and HF [1–4], and the characterization of the adducts between the alkali-metal cations and the F atoms of NF_3 as weakly bound complexes suggest the following considerations. If a cation M^+ has a thermochemical affinity for the fluorine atom which is significantly lower than the dissociation energy of the F_2N–F bond, ca. 60 kcal mol^{-1}, the interaction with the F atom(s) of NF_3 does not produce an appreciable structural reorganization, and leads to monocoordinated or dicoordinated structures which are essentially electrostatic complexes between M^+ and NF_3. This is the case, for example, of the alkali-metal ions Li^+, Na^+, and K^+, whose affinities for the F atoms of NF_3 regularly decrease from ca. 13 to ca. 5 kcal mol^{-1} and place NF_3 in the lower regions of the Li^+ [71], Na^+ [72], and K^+ [73] affinity scales. On the other hand, cations such as H^+, Be^+, and Mg^+, which have a strong affinity for the fluorine atom, form F_2N–FM^+ ions which feature strongly elongated N–F bonds. If the ionization potential (IP) of MF is higher than NF_2, 11.6 eV, these ions are predicted to have a F_2N^+–FM connectivity, which ensures the more favourable orientation of the MF dipole with respect to $NF_2{}^+$. This is the case, for example, of the F_2N^+–FH isomer (the IP of HF is 16.0 eV). On the other hand, if the IP of MF is lower than NF_2, the connectivity of the ions is expected to be F_2N–MF^+, which ensures the more favourable interaction between the positively charged M atom of MF^+ and the N atom of NF_2. This is the case of F_2N–BeF^+ and F_2N–MgF^+ (the IPs of BeF and MgF are 9.1 and 7.7 eV, respectively), whose stability is so large that the M^+ ion affinity of NF_3 becomes comparable, and even larger, than typically strong Lewis bases.

Acknowledgements

The authors wish to thank the Italian Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST) and the Consiglio Nazionale delle Ricerche (CNR) for financial support.

References

[1] J.J. Fisher, T.B. McMahon, J. Am. Chem. Soc. 110 (1988) 7599.

[2] F. Grandinetti, J. Hrusàk, D. Schröder, S. Karrass, H. Schwarz, J. Am. Chem. Soc. 114 (1992) 2806.

[3] K. Hiraoka, M. Nasu, S. Fujimaki, S. Yamabe, J. Phys. Chem. 99 (1995) 15822.

[4] F. Grandinetti, P. Cecchi, V. Vinciguerra, Chem. Phys. Lett. 281 (1997) 431.

[5] F. Grandinetti, V. Vinciguerra, J. Mol. Struct. (Theochem) 574 (2001) 185.

[6] F. Grandinetti, V. Vinciguerra, Int. J. Mass Spectrom. 216 (2002) 285.

[7] K. Pei, J. Liang, H. Li, J. Mol. Struct. 690 (2004) 159.

[8] S. Arulmozhiraja, T. Fujii, J. Phys. Chem. A 104 (2000) 9613.

[9] T. Fujii, M. Ogura, H. Jimba, Anal. Chem. 61 (1989) 1026.

[10] T. Fujii, M. Yashiro, H. Tokiwa, J. Am. Chem. Soc. 119 (1997) 12280.

[11] F. Ishii, Y. Kita, in: T. Nakajima, B. Žemva, A. Tressaud (Eds.), Advanced Inorganic Fluorides, Elsevier, Amsterdam, 2000, p. 629 (Chapter 19).

[12] D.T. Meshri, in: T. Nakajima, B. Žemva, A. Tressaud (Eds.), Advanced Inorganic Fluorides, Elsevier, Amsterdam, 2000, p. 673 (Chapter 20).

[13] F. Cacace, F. Grandinetti, F. Pepi, Angew. Chem. Int. Ed. Engl. 33 (1994) 123.

[14] M. Aschi, F. Cacace, F. Grandinetti, F. Pepi, J. Phys. Chem. 98 (1994) 2713.

[15] F. Cacace, F. Grandinetti, F. Pepi, J. Chem. Soc. Chem. Commun. (1994) 2173.

[16] F. Cacace, F. Grandinetti, F. Pepi, J. Phys. Chem. 98 (1994) 8009.

[17] F. Cacace, F. Grandinetti, F. Pepi, Inorg. Chem. 34 (1995) 1325.

[18] F. Grandinetti, F. Pepi, A. Ricci, Chem. Eur. J. 2 (1996) 495.

[19] M. Aschi, F. Grandinetti, V. Vinciguerra, Chem. Eur. J. 4 (1998) 2366.

[20] M. Aschi, F. Grandinetti, J. Mol. Struct. (Theochem) 497 (2000) 205.

[21] P. Antoniotti, S. Borocci, F. Grandinetti, Eur. J. Inorg. Chem. (2004) 1125.

[22] M. Trachtman, G.D. Markham, J.P. Glusker, P. George, C.W. Bock, Inorg. Chem. 37 (1998) 4421.

[23] R.K. Milburn, V.I. Baranov, A.C. Hopkinson, D.K. Bohme, J. Phys. Chem. A 102 (1998) 9803.

[24] J. Hinze, O. Friedrich, A. Sundermann, Mol. Phys. 96 (1999) 711.

[25] J.E. Reddic, M.A. Duncan, J. Chem. Phys. 110 (1999) 9948.

[26] S.S. Wesolowski, R.A. King, H.F. Schaefer III, M.A. Duncan, J. Chem. Phys. 113 (2000) 701.

[27] A. Andersen, F. Muntean, D. Walter, C. Rue, P.B. Armentrout, J. Phys. Chem. A 104 (2000) 692.

[28] T. Shoeib, R.K. Milburn, G.K. Koyanagi, V.V. Lavrov, D.K. Bohme, K.W.M. Siu, A.C. Hopkinson, Int. J. Mass Spectrom. 201 (2000) 87.

[29] E. Magnusson, J. Phys. Chem. A 105 (2001) 3881.

[30] R.K. Milburn, D.K. Bohme, A.C. Hopkinson, J. Mol. Struct. (Theochem) 540 (2001) 5.

[31] S. Yoshida, N. Okai, K. Fuke, Chem. Phys. Lett. 347 (2001) 93.

[32] S. Yoshida, K. Daigoku, N. Okai, A. Takahata, A. Sabu, K. Hashimoto, K. Fuke, J. Chem. Phys. 117 (2002) 8657.

[33] A.M. Sapse, J. Phys. Chem. A 106 (2002) 783.

[34] A. Gil, J. Bertran, M. Sodupe, J. Am. Chem. Soc. 125 (2003) 7461.

[35] D. Moran, H.L. Woodcock, Z. Chen, H.F. Schaefer III, P.v.R. Schleyer, J. Am. Chem. Soc. 125 (2003) 11442.

[36] S. Petrie, J. Phys. Chem. A 107 (2003) 10441.

[37] P. George, J.P. Glusker, G.D. Markham, M. Trachtman, C.W. Bock, Mol. Phys. 101 (2003) 2451.

[38] K. Daigoku, K. Hashimoto, J. Chem. Phys. 121 (2004) 3569.

[39] J.I. Lee, D.C. Sperry, J.M. Farrar, J. Chem. Phys. 121 (2004) 8375.

[40] X. Bu, C. Zhong, A.F. Jalbout, Chem. Phys. Lett. 387 (2004) 410.

[41] R.C. Dunbar, S. Petrie, J. Phys. Chem. A 109 (2005) 1411.

[42] C.S. Yeh, J.S. Pilgrim, K.F. Willey, D.L. Robbins, M.A. Duncan, Int. Rev. Phys. Chem. 13 (1994) 231.

[43] D. Bellert, W.H. Breckenridge, Chem. Rev. 102 (2002) 1595.

[44] M.J. Frish, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzevski, J.A. Montgomery, R.E. Stratman, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.7, Gaussian Inc., Pittsburgh, PA, 1998.

[45] MOLPRO is a package of ab initio programs written by H.-J. Werner and P.J. Knowles, with contributions from R.D. Amos, A. Bernhadsson, A. Berning, P. Celani, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A.W. Lloyd, S.J. McNicholas, F.R. Manby, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schatz, H. Stoll, A.J. Stone, R. Tarroni, and T. Thorsteinsson.

[46] A.D. McLean, G.S. Chandler, J. Chem. Phys. 72 (1980) 5639.

[47] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72 (1980) 650.

[48] T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.v.R. Schleyer, J. Comput. Chem. 4 (1983) 294.

[49] M.J. Frish, J.A. Pople, J.S. Binkley, J. Chem. Phys. 80 (1984) 3265.

[50] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frish, J. Phys. Chem. 98 (1994) 11623.

[51] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[52] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.

[53] C. Hampel, K. Peterson, H.-J. Werner, Chem. Phys. Lett. 190 (1992) 1.

[54] P.J. Knowles, C. Hampel, H.-J. Werner, J. Chem. Phys. 99 (1993) 5219.

[55] J.D. Watts, J. Gauss, R.J. Bartlett, J. Chem. Phys. 98 (1993) 8718.

[56] D.A. Mc Quarry, Statistical Mechanics, Harper & Row, New York, 1973.

[57] S. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.

[58] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Oxford University Press, Oxford, 1990.

[59] J. Cioslowski, S.T. Mixon, J. Am. Chem. Soc. 113 (1991) 4142.

[60] J. Cioslowski, A. Nanayakkara, Chem. Phys. Lett. 219 (1994) 151.

[61] AIM2000, designed by F. Biegler-König, University of Applied Sciences, Bielefeld, Germany (http://www.aim2000.de/).

[62] J. Sheridan, W. Gordy, Phys. Rev. 79 (1950) 513.

[63] Thermochemical data are taken from: P.J. Linstrom, W.G. Mallard (Eds.), NIST Chemistry Webbook, NIST Standard Reference Database Number 69, National Institute of Standard and Technology, Gaithersburg, MD 20899, March 2003 (http://webbook.nist.gov/).

[64] F.R. Ornellas, F.B.C. Machado, O. Roberto-Neto, Mol. Phys. 77 (1992) 1169.

[65] A. Papakondylis, A. Mavridis, Chem. Phys. Lett. 216 (1993) 167.

[66] J. Czernek, O. Živny, Chem. Phys. 303 (2004) 137.

[67] J.M. Dyke, T.G. Wright, Chem. Phys. Lett. 169 (1990) 138.

[68] At the B3LYP level of theory, with all the employed basis sets, we have also located an energy minimum of F_2N–F–Mg^+ connectivity, which resulted less stable than isomer **6** by ca. 22 kcal mol^{-1}. However, we could not confirm the existence of this isomer at the RCCSD/6-311G(d) level of theory.

[69] H. Partridge, S.R. Langhoff, C.W. Bauschlicher Jr, J. Chem. Phys. 84 (1986) 4489.

[70] C.W. Bauschlicher Jr, M. Sodupe, H. Partridge, J. Chem. Phys. 96 (1992) 4453.

[71] P. Burk, I.A. Koppel, I. Koppel, R. Kurg, J.-F. Gal, P.-C. Maria, M. Herreros, R. Notario, J.-L.M. Abboud, F. Anvia, R.W. Taft, J. Phys. Chem. A 104 (2000) 2824.

[72] P.B. Armentrout, M.T. Rodgers, J. Phys. Chem. A 104 (2000) 2238.

[73] J.K.-C. Lau, C.H.S. Wang, P.S. Ng, F.M. Siu, N.L. Ma, C.W. Tsang, Chem. Eur. J. 9 (2003) 3383.