

Structure and Properties of NH_5^{2+} : A Dication with Two 2-Electron 3-Center Bonds

JANET E. DEL BENE,¹ JOHN D. WATTS,² RODNEY J. BARTLETT²

¹Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555

²Quantum Theory Project, P.O. Box 118435, University of Florida, Gainesville, FL 32611

Received 30 March 1998; revised 1 July 1998; accepted 13 July 1998

ABSTRACT: The dication NH_5^{2+} has been studied by state-of-the-art quantum chemical techniques. NH_5^{2+} is a square-based pyramid with C_{4v} symmetry. The apical H is bonded to N with a 2-electron covalent bond, while the other H atoms are bonded to N through degenerate 2-electron 3-center bonds. No other local minimum exists on the potential energy surface. A C_{2v} transition state linking equivalent C_{4v} structures is only 1.35 kcal mol⁻¹ higher in energy. The barrier to deprotonation is 26.4 kcal mol⁻¹. © 1998 John Wiley & Sons, Inc. *Int J Quant Chem* 70: 1003–1007, 1998

Key words: dications; coupled-cluster calculations; penta coordinate nitrogen

Introduction

Although the dication NH_5^{2+} has not been observed experimentally, it is an interesting species for several reasons.

1. NH_5^{2+} is isoelectronic with the pentahydrides BH_5 and CH_5^+ , which have been the subjects of several theoretical [1] and experimental [2] studies.

Correspondence to: J. D. Watts.

Contract grant sponsor: U.S. Air Force Office of Scientific Research.

Contract grant number: AFOSR-F 49620-95-1-0130.

2. NH_5^{2+} continues the known isoelectronic series NH_2^- , NH_3 , and NH_4^+ , which we examined recently [3].
3. Olah and Rasul [4] have noted that NH_5^{2+} is isolobal with the gold complex $[(\text{C}_6\text{H}_5)_3\text{PAu}]_5\text{N}^{2+}$ [5], which features a trigonal bipyramidal nitrogen.

In this study we report a series of coupled-cluster calculations with extended basis sets on NH_5^{2+} . The aims of this work were to determine the structure and energetics of local minima and other important stationary points, to compute vibrational frequencies, which might be useful for future experimental studies, to analyze the bonding, and to compare with isoelectronic analogs. Since

experimental study of small multiply charged species is very difficult, high-quality calculations may provide useful data, as well as valuable insight into the bonding in these species. During the final stages of this work, Olah et al. [6] reported an attempt to generate NH_5^{2+} and $(\text{CH}_3)_4\text{NH}^{2+}$ by protonating NH_4^+ and $(\text{CH}_3)_4\text{N}^+$ in superacid media, but these were not successful. They also reported some ab initio calculations on NH_5^{2+} with the MBPT(2) and QCISD methods and 6-31G** and 6-311G** basis sets. These calculations are much less extensive than the ones reported in this work, but both studies lead to similar structures and energetics.

Computational Methods

Calculations were performed with the ACES II program [7, 8]. The methods used were second-order many-body perturbation theory [MBPT(2)] and coupled-cluster singles and doubles with non-iterative triples [CCSD(T)] [9]. The basis sets used were the augmented correlation-consistent polarized valence triple-zeta basis set (aug-cc-pVTZ) [10], and this basis set without diffuse functions on hydrogen (denoted aug'-cc-pVTZ). Geometries were determined at the MBPT(2)/aug-cc-pVTZ, CCSD(T)/aug-cc-pVTZ, and CCSD(T)/aug'-cc-pVTZ levels. Since the CCSD(T) structures of NH_5^{2+} computed with the two basis sets are essentially identical, only CCSD(T)/aug'-cc-pVTZ harmonic vibrational frequencies were computed. Geometry optimizations of BH_5 and CH_5^+ were performed at the MBPT(2)/aug-cc-pVTZ level for comparison. In all calculations, the 1s electrons of the nonhydrogen atom (B, C, or N) were not correlated. Spherical harmonic *d* and *f* functions were used throughout.

Results and Discussion

The potential energy surface of NH_5^{2+} was first searched at the MBPT(2)/aug-cc-pVTZ level. Stationary points were then further investigated at the CCSD(T)/aug-cc-pVTZ level. Unless otherwise stated, energy differences quoted below are from CCSD(T)/aug-cc-pVTZ calculations. The stationary points on the NH_5^{2+} surface are shown in Figure 1, and their total energies, along with those of several other relevant species, are given in Table I.

The lowest energy structure of NH_5^{2+} (**1**) has C_{4v} symmetry, and is a local minimum. The geometries of **1** obtained at three levels of theory are reported in Table II. The next lowest energy stationary point is **2**. This is a transition structure of C_{2v} symmetry, which is only 1.35 kcal mol⁻¹ higher in energy than **1**. Structure **2** is the saddle point for interchange of apical and basal hydrogen atoms in **1**, and so connects equivalent C_{4v} structures. A second transition state of importance is that for deprotonation of NH_5^{2+} , which is structure **3**. As expected, decomposition to $\text{NH}_4^+ + \text{H}^+$ is highly exothermic (98 kcal mol⁻¹), but the barrier to deprotonation is significant (26.4 kcal mol⁻¹). Elongation of one of the basal N—H bonds leads to the transition state for deprotonation. This transition state was expected to have only C_s symmetry, since elongation of one of the four equivalent N—H bonds reduces the symmetry to C_s . However, closer examination showed it to have C_{3v} symmetry, as reported by Olah et al. [6], which is the highest symmetry possible for $\text{NH}_4^+ + \text{H}^+$. Elongation of the apical N—H bond appears to lead to unfavorable homolytic dissociation, rather than deprotonation. The trigonal bipyramidal structure of NH_5^{2+} (**4**) is only 2.7 kcal mol⁻¹ higher in energy than **1**, but it is neither a local minimum nor a transition state. It has a doubly degenerate imaginary frequency. This mode leads to the C_{4v} structure, the two axial H atoms of **4** become basal H atoms in **1**, and one of the equatorial H atoms in **4** becomes the apical H atom in **1**. Structure **4** provides another pathway for interchange of apical and basal H atoms of **1**.

In the equilibrium structure of NH_5^{2+} (**1**), four of the H atoms (H_b) are at the base of a pyramid, and the fifth H atom (H_a) is at the apex. All of the N—H distances are similar. The N— H_a distance is slightly smaller than the N— H_b distance. The shortest H—H distance is 1.46 Å, which is the distance between adjacent basal H atoms. By no means, then, is NH_5^{2+} a complex between NH^{2+} and H_2 . What, therefore, is the bonding in C_{4v} NH_5^{2+} ? A qualitative and plausible description can be obtained by examining the occupied molecular orbitals (MOs). The most stable valence MO in the MO in the C_{4v} structure has a_1 symmetry and is essentially the 2s N orbital, but is largely non-bonding. Higher in energy are the degenerate *e* orbitals, which form the bonds between the N and the four equivalent H_b atoms. If one pair of H_b atoms lies along the *x* axis and the other along the

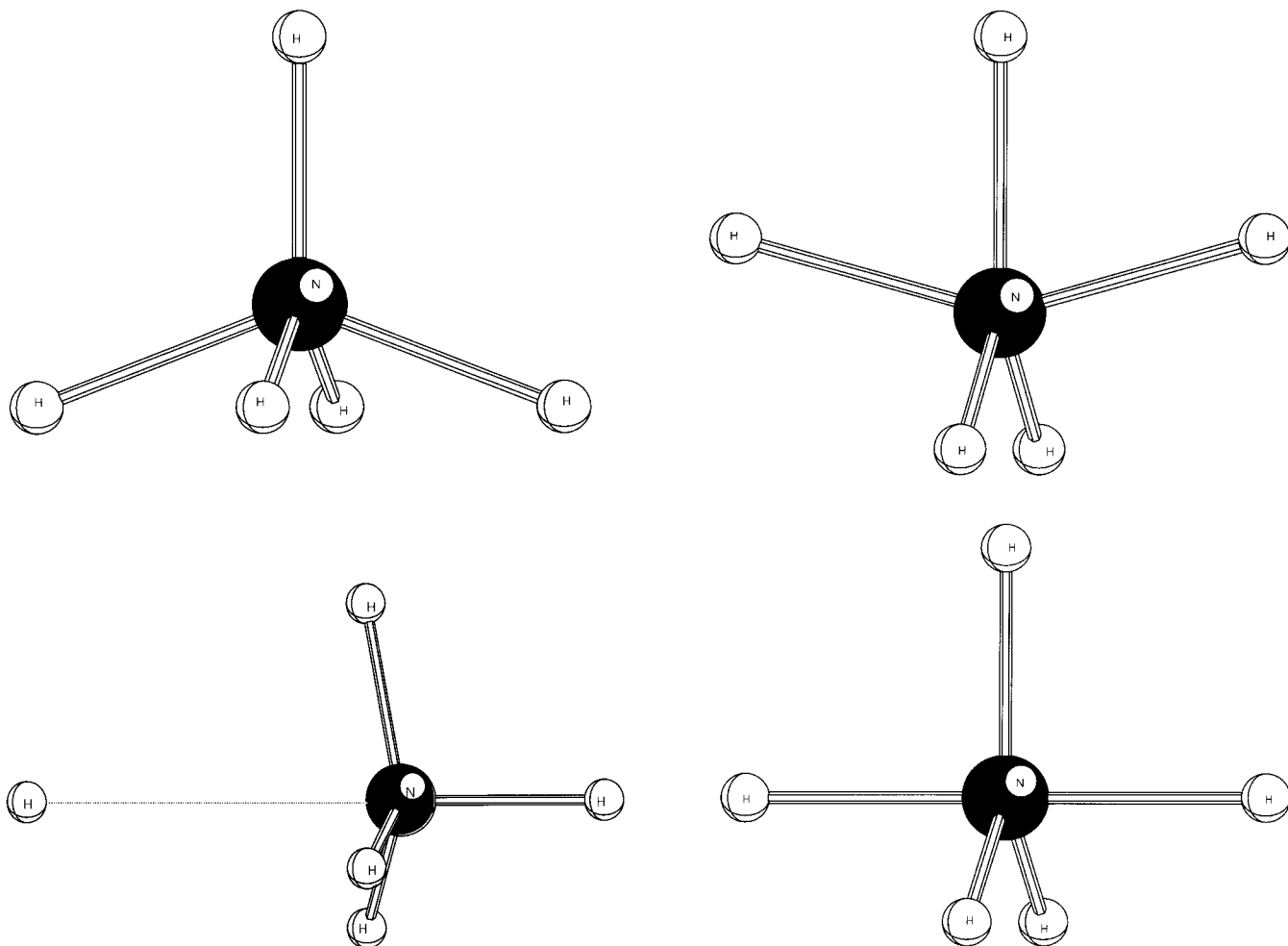


FIGURE 1. Four stationary points on the NH_5^{2+} potential energy surface. The point group symmetries of **1**, **2**, **3**, and **4** are C_{4v} , C_{2v} , C_{3v} , and D_{3h} , respectively.

y axis, one e orbital consists largely of an N p_x orbital overlapping with an antisymmetric combination of a pair of H_b s orbitals, and the other is of the same type, but with the N p_y orbital and the s orbitals of the other pair of H_b atoms. Since the N

atom lies 0.4 \AA above the base of the pyramid (Table II), the bonds between the N and basal H atoms may be described as two bent 2-electron, 3-center bonds. The highest occupied MO, which is almost degenerate with the e MOs, has a_1 symme-

TABLE I
Total energies (Hartrees) and relative energies (kcal mol^{-1}) of stationary points **1**, **2**, **3**, and **4** of NH_5^{2+} and some other relevant species.^a

	Symmetry	MBPT(2)	CCSD(T)
NH_5^+ (1)	C_{4v}	-56.64071 (0.0)	-56.66145 (0.0)
NH_5^{2+} (2)	C_{2v}	-56.63842 (1.4)	-56.65930 (1.3)
NH_5^{2+} (3)	C_{3v}	-56.59862 (26.4)	-56.61935 (26.4)
NH_5^{2+} (4)	D_{3h}	-56.63959 (2.6)	-56.65720 (2.7)
NH_4^+	T_d	-56.79615 (-97.5)	-56.81802 (-98.2)
NH_3^+	D_{3h}	-55.22365	-55.24923
H_2	$D_{\infty h}$	-1.16502	-1.17264

^a Energies obtained with the aug-cc-pVTZ basis set.

TABLE II
Distances (Å) and angles (°) in C_{4v} NH_5^{2+} .

	MBPT(2) / aug-cc-pVTZ	CCSD(T) / aug-cc-pVTZ	CCSD(T) / aug'-cc-pVTZ
$r(N-H_a)^a$	1.0517	1.0524	1.0522
$r(N-H_b)^b$	1.1068	1.1074	1.1072
$r(N-X)^c$	0.4063	0.4068	0.4066
$r(H-H)^d$	1.4559	1.4566	1.4564
$\theta(H_aNH_b)^e$	111.5	111.6	111.5

^a The distance from N to the apical H atom (H_a).

^b The distance from N to one of the basal H atoms (H_b).

^c The perpendicular distance from N to the basal plane.

^d The distance between adjacent basal H atoms.

^e The H_aNH_b angle.

try and constitutes the bonding MO between the N and the apical H atom.

The bonding in C_{4v} NH_5^{2+} contrasts strongly with that in BH_5 and CH_5^+ . BH_5 is best described as a species in which H_2 is attached to an almost unperturbed BH_3 molecule, with the complex stabilized by overlap of the H_2 bonding orbital and the empty p orbital on BH_3 . At the MBPT(2)/aug-cc-pVTZ level, the H_2 bond length in BH_5 is 0.79 Å, compared with 0.74 Å in free H_2 . Similarly, CH_5^+ can be described as a complex between CH_3^+ and H_2 , but in this case the interaction is stronger, and the H—H distance (0.98 Å) is significantly larger than in free H_2 . That the nature of the bonding in NH_5^{2+} is unlike that in BH_5 and CH_5^+ is further illustrated by a comparison of the energies required to remove H_2 . In the series BH_5 , CH_5^+ , NH_5^{2+} , the energy for removal of H_2 increases considerably, as expected. At the MBPT(2)/aug-cc-pVTZ level of theory, ΔH° val-

ues for the reactions $BH_5 \rightarrow BH_3 + H_2$, $CH_5^+ \rightarrow CH_3^+ + H_2$, and $NH_5^{2+} \rightarrow NH_3^+ + H_2$ are 0.6, 43.7, and 115.5 kcal mol⁻¹, respectively. Are there stable C_{4v} structures for BH_5 and CH_5^+ and how do these compare with the equilibrium C_s structures? At MBPT(2)/aug-cc-pVTZ, C_{4v} structures of BH_5 and CH_5^+ are 18 and 3 kcal mol⁻¹ less stable than the C_s structures and are not local minima.

CCSD(T)/aug'-cc-pVTZ and MBPT(2)/aug-cc-pVTZ harmonic frequencies and infrared intensities for the C_{4v} structure of NH_5^{2+} are given in Table III, along with approximate descriptions of the normal modes. There are no low-frequency vibrational modes in NH_5^{2+} . This suggests that if this dication could be formed, it should be stable at low temperature. Moreover, the lowest frequency mode does not lead to decomposition. Rather, it reduces the symmetry to C_{2v} , and is the initial motion toward the C_{2v} transition state for exchange of apical and basal H atoms. The most

TABLE III
MBPT(2) / aug-cc-pVTZ and CCSD(T) / aug'-cc-pVTZ harmonic frequencies (cm⁻¹) and infrared intensities (km mol⁻¹) for C_{4v} NH_5^{2+} .^a

Symmetry	MBPT(2)		CCSD(T)		Description
	ω	I	ω	I	
b_2	620	0	624	0	Antisymmetric H_aNH_b , bend
e	674	930	643	936	H_bNH_b "rocking" motion
a_1	1352	266	1352	263	Symmetric H_aNH_b bend ("umbrella" mode)
e	1536	75	1538	77	H_aNH_b bend
b_1	1627	0	1618	0	In-plane H_bNH_b bend ("scissor")
b_2	2369	0	2368	0	Antisymmetric N— H_b stretch
e	2653	2041	2654	1963	N— H_b stretch
a_1	2755	148	2755	143	Symmetric N— H_b stretch
a_1	3146	471	3144	441	N— H_a stretch

^a H_a and H_b are the apical and basal H atoms.

intense band in the infrared spectrum of NH_5^{2+} is predicted to occur around 2650 cm^{-1} . This band is due to a degenerate antisymmetric stretching mode involving the basal H atoms and N. This mode reduces the symmetry to C_s , which is the initial motion along the pathway leading to deprotonation.

Finally, it should be noted that although C_{4v} NH_5^{2+} is a local minimum, exchange of hydrogen atoms is likely to be rapid, as the transition state is of low energy and tunneling may be important. Accordingly, except on very short time scales, the H atoms will be effectively equivalent. Some of these features of the behavior of CH_5^+ have previously been noted [1(d), (e)], and there have been a few dynamical studies of that system [11]. Unlike CH_5^+ , however, NH_5^{2+} does not have any very low vibrational frequencies.

ACKNOWLEDGMENTS

This work has been supported by the U.S. Air Force Office of Scientific Research (Grant No. AFOSR-F49620-95-1-0130). The Ohio Supercomputer Center is thanked for provision of facilities for the development of the ACES II program system and for some of the calculations. Kenneth J. Wilson is thanked for preparing the figures.

References

- (a) J. F. Stanton, W. N. Lipscomb, and R. J. Bartlett, *J. Am. Chem. Soc.* **111**, 5173 (1989). (b) P. R. Schreiner, H. F. Schaefer III, and P. von R. Schleyer, *J. Chem. Phys.* **101**, 7625 (1994). (c) J. D. Watts and R. J. Bartlett, *J. Am. Chem. Soc.* **117**, 825 (1995). (d) P. R. Schreiner, S.-J. Kim, H. F. Schaefer III, and P. von R. Schleyer, *J. Chem. Phys.* **99**, 3716 (1993). (e) H. Müller, W. Kutzelnigg, J. Noga, and W. Klopper, *J. Chem. Phys.* **106**, 1863 (1997).
- (a) T. J. Tague and L. Andrews, *J. Am. Chem. Soc.* **116**, 4970 (1994). (b) D. W. Boo and Y. T. Lee, *Chem. Phys. Lett.* **211**, 358 (1993). (c) D. W. Boo and Y. T. Lee, *J. Chem. Phys.* **103**, 514 (1995).
- R. J. Bartlett, J. E. Del Bene, S. A. Perera, and R. P. Mattie, *J. Mol. Struct. (THEOCHEM)* **400**, 157 (1997).
- G. A. Olah and G. Rasul, *J. Am. Chem. Soc.* **118**, 12922 (1996).
- A. Grohmann, J. Riede, and H. Schmidbaur, *Nature* **345**, 140 (1990).
- G. A. Olah, A. Burrichter, G. Rasul, and G. K. S. Prakash, *J. Am. Chem. Soc.* **119**, 4594 (1997).
- J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett, *Int. J. Quant. Chem. Symp.* **26**, 879 (1992).
- ACES II is a program product of the Quantum Theory Project, University of Florida. Authors: J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balková, D. E. Bernholdt, K.-K. Baeck, P. Rozyczko, H. Sekino, C. Huber, and R. J. Bartlett. Integral packages included are VMOL (J. Almlöf and P. R. Taylor); VPROPS (P. R. Taylor); ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, and P. R. Taylor).
- (a) G. D. Purvis III and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982). (b) M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, *J. Chem. Phys.* **83**, 4041 (1985). (c) K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- (a) T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989). (b) R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *Ibid.*, **96**, 6796 (1992).
- (a) P. R. Bunker, *J. Mol. Spectrosc.* **176**, 297 (1996). (b) D. Marx and M. Parrinello, *Nature* **375**, 216 (1995). (c) M. Kolbuszewski and P. R. Bunker, *J. Chem. Phys.* **105**, 3649 (1996).