On the Bonding Nature of the $\text{N}_5^+ (= \text{N}(\text{N}_2)_2^+)$ Cation and Related Species $\text{N} (\text{CO})_x^+$, $\text{N} (\text{NH}_3)_x^+$, and $\text{NR}_x^+$, $x = 1, 2$ and $R = \text{He, Ne, Ar, Kr}$. Do We Really Need the Resonance Concept?

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We attempt to elucidate the bonding nature of the isoelectronic and isovalent cations $\text{N}_5^+ (= \text{N}(\text{N}_2)_2^+)$ and $\text{N} (\text{CO})_x^+$, the salts of which have been recently isolated. By performing coupled-cluster RCCSD(T) calculations, we argue against the “resonance” bonding approach as redundant, and we claim that the bonding in the aforementioned species is naturally explained by realizing that the in situ central nitrogen ($\text{N}^+$) finds itself in the first excited 1 $\text{D}$ state, thus forming two equivalent dative bonds with $\text{N}_2$ and $\text{CO}$, respectively. To further support our position, we have also studied at the same level of theory the molecules $\text{NNH}_3^+$, $\text{N}(\text{NH}_3)_2^+$, $\text{NR}_x^+$, and $\text{NR}_x^+$, where $R = \text{He, Ne, Ar, and Kr}$. It is predicted that the $\text{N}(\text{NH}_3)_3^+$ system is clearly isolable, whereas under certain conditions, $\text{NKR}_2^+$ (and perhaps $\text{NXe}_2^+$) could also be “trapped” experimentally.

1. Introduction

In 1999, two rather exotic molecular systems were isolated by two independent groups, namely, the isoelectronic and isovalent cations $\text{N}_5^+ (= \text{N}(\text{N}_2)_2^+)$ and $\text{N} (\text{CO})_x^+$. Remarkably, both papers were submitted to the same journal within a time interval of 7 days. The $\text{N}_5^+$ ion was trapped as a $\text{N}_5^+ \text{AsF}_6^-$ salt and described as “a white solid sparingly soluble in anhydrous HF, marginally stable at 22 °C and which can be stored for weeks at −78 °C without noticeable decomposition”. Very recently, the Christe group announced the preparation of two new $\text{N}_5^+$ salts, $\text{N}_5^+ \text{SbF}_6^-$ and $\text{N}_5^+ \text{Sb}_2 \text{F}_{11}^-$, showing surprisingly thermal stability: they decompose at 70 °C, showing also relative stability with respect to impact. The X-ray analysis of the $\text{N}_5^+ \text{Sb}_2 \text{F}_{11}^-$ crystals revealed the following V-shaped ($C_{\text{V}}$) structure for the $\text{N}_5^+$ cation

\[ \text{N}_5^+ \quad \text{(1)} \]

Values in square brackets are theoretical predictions at the CCD/6-31G(d, p) level of theory.

Although the discovery of a stable $\text{N}(\text{CO})_2^+$ species is of significant academic importance, its isolation did not attract the attention of the chemical community as in the case of the $\text{N}_5^+$ species. Perhaps because the announcement of the existence of a stable $\text{N}_5^+$ molecule was so unexpected that it completely eclipsed the important fact of the isolation of an isoelectronic, isovalent, and identically bonded (vide infra) to the $\text{N}_5^+$ system or, perhaps, because $\text{N}(\text{CO})_2^+$ had already been observed in 1992 in the gas phase by mass spectrometric methods.

As expected, after the isolation of the $\text{N}_5^+$ species, several ab initio and DFT calculations followed, focusing mainly on the geometry and stability of $\text{N}_5^+$, and confirming in essence the results of the original publication. However, what has not been resolved yet, at least according to the present authors, is the bonding nature of $\text{N}_5^+$ and related isoelectronic (like $\text{N}(\text{CO})_2^+$) or isovalent (like $\text{N}(\text{CS})_2^+$, for instance) molecules. As a matter of fact, this is exactly what motivated the present report, that is, a clear understanding of the bonding mechanism of $\text{N}_5^+$ and similar species, based exclusively on calculable (or measurable) properties and not on vague or ill-defined concepts, like “resonance”. Toward that goal, we have performed accurate-enough, first principles calculations on a series of similarly

\[ \text{N}_5^+ \quad \text{(2)} \]
bonded systems N(XY)+, NR+ and N(NH3)+ where XY = N2, CO, R = He, Ne, Ar, or Kr, and x = 1, 2, and their fragments, charged or otherwise (but see below).

2. Chemical Insights

As it was alluded in the Introduction, the favorable explanation concerning the “understanding” of the bonding and stability of N5+ is the historically useful but admittedly not well-defined idea of resonance.14 In the recent article by Christe and co-workers,3 the bonding in N5+ is rationalized by the following series of resonance (sometimes called “canonical”) structures:

Klapoštke15 explains the stability and bonding of N5+ by employing “increased-valence” structures of the type

introduced by Harcourt,16 where thin bonds on the right show fractional electron pair bonds. In another article by Ponec et al.,10 the N5+ bonding is presumably understood by introducing the following “new” resonance scheme.

We believe that it is bad philosophy to try to comprehend something, here the bonding of the N5+ cation, with something ill-defined, here the concept of resonance. Schemes 3–5, by any means, cannot be considered as a theory or as a model of explaining the bonding of molecules or as having any predictive power. The rationalization comes after the fact (“hindsight”) which is “fitted” to the resonance structures, and of course, a new resonance form can always be added to assist the “explanation” in a completely ad hoc manner.

We can imagine now that the N5+ cation is composed of N+ and two dinitrogen (N2) species and formed by the sequence of reactions

The two N–N bonds of the N5+ cation are equal (in the past, people theorized on an unsymmetrical N5+),17 because of the participation in the bonding, by symmetry, of the mirror image of the vbl icon in Scheme 6. We also remind that the ionization energies (IE) of N(6S) and N2(X1Σg+) are 14.5418 and 15.5819 eV, respectively; therefore, the asymptotic energy fragments of N5+(X3Σg−) are indeed N+(P) + N2(X1Σg+) and not N(6S) + N2(X3Σg−). Clearly, a second N2 cannot be bonded to N5+(X3Σg−), but it can “stick” to it electrostatically by a few kcal/mol, forming a triplet N5+·N2 state.7,20 However, exciting the X3Σg− state of N5+ to âΔg state, ΔE(âΔg → X3Σg−) = 1.2 eV (vide infra), creates immediately the proper conditions for the bonding of a second N2(X1Σg+) molecule, as it is obvious from the following vbl diagram:

Again, the channel N5(3Π) + N2+(X2Σg+) is precluded because the IE of N2(X1Σg+) is larger than that of N5.19,29

Alternatively, we can imagine that two N2(X1Σg+) moieties are bonded to the N5+(1D; 2s2p2) state, 1.888 eV (=43.53 kcal/mol) above the ground N5+(P) state:18

Scheme 7, parts a and b, rationalizes and predicts the bonding features of N5+, i.e., that (a) the terminal N–N bonds should remain practically intact (triple bonded), (b) the bond to the central nitrogen is, in essence, a “dative” single bond, (c) the charge of the central atom should diminish drastically or even acquire some negative character, (d) the in situ central atom finds itself to the excited N5+(1D) state, and (e) it dictates the, in general, bent structure of N5+. In addition, vbls 7a and 7b anticipate that by pulling apart N5+ according to N5+ → N5+ + N2 we should find N5+ in its âΔg state, or by pulling away the two N2 molecules in a symmetrical fashion, N5+ → N5+ + 2N2, N5+ should be found in a 1D (s2p3) state. Finally, this harpoon-like (dative) bonding clearly implies that the N5+ species can be “ripped apart” using a single reference calculational approach like a coupled-cluster (CC) or perturbational (MPn) technique or even at the Hartree–Fock level. Of course, the correct description of N5+ in a pure 1D state is not feasible at a single-reference level, but we consider this as a minor point for the purpose of the present report.

Bonding mechanisms exemplified through Schemes 6 and 7a,b can be repeated but using the molecules CO (X1Σg+; isoelectronic and isovalent to N2), CS (X1Σg+; isovalent to N2), and NH3(31A1), instead of N2, thus creating the systems NXY+, N(NXY)+ (where XY = CO, CS) and NH3N+, N(NH3)+, in complete analogy to the N5+(=N(N2))2+ species. Within the same bonding model, we can also incorporate the molecules NR+ and NR2+, where R = He, Ne, Ar, and Kr.21 Indeed, what does one expect to be the bonding mechanism in the
NR\textsuperscript{+} and NR\textsubscript{2}\textsuperscript{+} rare gas series? The following vbL diagrams are revealing:

![Diagram](image)

The realization of Schemes 8 and 9 depends on the IE = 14.54 eV of N(4S)\textsuperscript{18} vs the IE of R(1S) = He, Ne, Ar, and Kr, 24.580, 21.59, 17.755, and 13.996 eV, respectively;\textsuperscript{18} therefore, Scheme 9 takes place only for the Kr atom. To the NR\textsuperscript{+} X\Sigma\textsuperscript{−} state, no (neutral) second R atom could be bound “chemically”, but this can be achieved by exciting the NR\textsuperscript{+} species to the a\Delta state, in complete analogy to Scheme 7a,b.

The calculations that follow for the series N(N\textsubscript{2})\textsuperscript{+}, Ni(CO)\textsuperscript{+}, N(NH\textsubscript{3})\textsuperscript{+}, and NR\textsubscript{2}\textsuperscript{+}, x = 1, 2 and R = He, Ne, Ar, and Kr, are a very strong indication that the above discussion is on the right track, dismissing at the same time the resonance rationalization as redundant and, therefore, in accordance to Ockham’s razor dictum.\textsuperscript{22} The system(s) N(CS)\textsubscript{x}\textsuperscript{+}, x = 1, 2 are not examined presently because of the vicissitudes of the CS molecule and its relatively low ionization energy; a separate study is intended to be devoted to the N(CS)\textsubscript{x}\textsuperscript{+} molecule(s). Suffice it to say at this point that N(CS)\textsubscript{2}\textsuperscript{+} is a linear (X\Delta\textsuperscript{1}) but very floppy molecule.\textsuperscript{23}

For the aforementioned molecular systems, we have performed valence RCCSD(T) calculations in conjunction with correlation-consistent basis sets.\textsuperscript{24} By “parenthesis T” it is meant the approximate and practically lowest order noniterative correction to the CCSD (S = T\textsubscript{1} and D = T\textsubscript{2}) energy from connected triples (T\textsubscript{3}). For all molecules studied, we report total energies, geometries, dissociation energies, and potential energy curves of the processes N\textsubscript{1}\textsuperscript{+} → N\textsuperscript{+} + N\textsubscript{2}, NCO\textsuperscript{+} → N\textsuperscript{+} + CO, N\textsubscript{5}\textsuperscript{+} → N\textsuperscript{+} + 2N\textsubscript{2}, and N(CO)\textsubscript{2}\textsuperscript{+} → N\textsuperscript{+} + 2CO at the RCCSD(T)/cc-pVTZ level of theory. In addition, and only for the isoelectronic and isovalent species N(N\textsubscript{2})\textsuperscript{+} and N(CO)\textsubscript{2}\textsuperscript{+}, geometrical structures and bond energies were determined at the RCCSD(T)/cc-pVQZ level.

### Table 1: Energies E (hartree), Bond Lengths \(r_e\) (Å), and Ionization Energies IE (eV) of Various Atomic and Molecular Species at the RCCSD(T)/cc-pVTZ Level of Theory (Experimental Values in Parentheses)

<table>
<thead>
<tr>
<th>Species</th>
<th>E</th>
<th>IE\textsuperscript{a}</th>
<th>Species</th>
<th>E</th>
<th>IE\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(4S)</td>
<td>54.51433</td>
<td>14.429 (14.54)</td>
<td>N\textsubscript{2}(X\Sigma\textsuperscript{+})</td>
<td>109.37394</td>
<td>1.104 (1.0977)</td>
</tr>
<tr>
<td>N(4D)</td>
<td>54.41354</td>
<td></td>
<td>N\textsubscript{2}(X\Sigma\textsuperscript{+})</td>
<td>108.80697</td>
<td>1.123 (1.1164)</td>
</tr>
<tr>
<td>N(4P)</td>
<td>53.98406</td>
<td></td>
<td>CO(X\Sigma\textsuperscript{+})</td>
<td>113.15558</td>
<td>1.136 (1.1283)</td>
</tr>
<tr>
<td>He(S)</td>
<td>2.900232</td>
<td>24.526 (24.590)</td>
<td>NH\textsubscript{3}(X\Delta\textsubscript{1})</td>
<td>56.47320</td>
<td>1.014 (1.0124)</td>
</tr>
<tr>
<td>He(2S)</td>
<td>1.998921</td>
<td></td>
<td>NH\textsubscript{3}(X\Delta\textsubscript{1})</td>
<td>56.10527</td>
<td>1.022 (1.014)</td>
</tr>
<tr>
<td>Ne(S)</td>
<td>128.80245</td>
<td>21.303 (21.559)</td>
<td>CO(X\Sigma\textsuperscript{+})</td>
<td>113.18791</td>
<td>1.131</td>
</tr>
<tr>
<td>Ne(2P)</td>
<td>128.01957</td>
<td></td>
<td>CO(X\Sigma\textsuperscript{+})</td>
<td>113.18791</td>
<td>1.131</td>
</tr>
<tr>
<td>Ar(S)</td>
<td>527.04307</td>
<td>15.550 (15.755)</td>
<td>CO(X\Sigma\textsuperscript{+})</td>
<td>113.18791</td>
<td>1.131</td>
</tr>
<tr>
<td>Ar(2P)</td>
<td>526.47163</td>
<td></td>
<td>CO(X\Sigma\textsuperscript{+})</td>
<td>113.18791</td>
<td>1.131</td>
</tr>
<tr>
<td>Kr(S)</td>
<td>2752.24498</td>
<td>13.923 (13.996)</td>
<td>CO(X\Sigma\textsuperscript{+})</td>
<td>112.67443</td>
<td>1.118</td>
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<tr>
<td>Kr(2P)</td>
<td>2751.7333</td>
<td></td>
<td>CO(X\Sigma\textsuperscript{+})</td>
<td>112.67443</td>
<td>1.118</td>
</tr>
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</table>

\textsuperscript{a} Experimental values from ref 18. \textsuperscript{b} Experimental values from ref 19. \textsuperscript{c} Calculated (expt.) ÐHNH angle 105.6° (106.7°), with experimental values from ref 26. \textsuperscript{d} Experimental value from ref 27. \textsuperscript{e} ÐHNH angle, by symmetry 120°. \textsuperscript{f} Experimental value from ref 28. \textsuperscript{g} At the RCCSD(T)/cc-pVQZ level.

All of our calculations were performed with the MOLPRO 2000.1 package.\textsuperscript{25}

### 3. Results and Discussion

Table 1 collects absolute energies and IE (ionization energies) of a series of atomic species involved in the molecules studied, as well as total energies, bond lengths \(r_e\), and IEs of the molecules N\textsubscript{2}(X\Sigma\textsuperscript{+}), CO(X\Sigma\textsuperscript{+}), NH\textsubscript{3}(X\Delta\textsubscript{1}), and their cations, at the RCCSD(T) level of theory. We observe that \(r_e\) and IE values are in acceptable agreement with existing experimental results, at least for the purpose of the present work. The largest deviations are observed in the separation energies N\textsubscript{2}(2D) → N\textsubscript{2}(1S) = 2.743 (2.683) and N\textsubscript{2}(2P) → N\textsubscript{2}(1P) = 2.104 (2.054) eV (values in parentheses have been calculated at the cc-pVQZ level), as compared to the experimental values 2.384 and 1.888 eV,\textsuperscript{18} respectively.

Table 2 lists total energies, \(D_e\) values, with respect to the N\textsuperscript{+} + XY/R and N + XY\textsuperscript{+}R\textsuperscript{+} channels, geometries, and (Hartree–Fock) Mulliken charges of the molecules N(XY/R)\textsuperscript{+} (where XY = N\textsubscript{2}, CO and R = He, Ne, Ar, Kr) and NN\textsubscript{H}\textsuperscript{+}, in their ground triplet and singlet states, as well as energy gaps between singlets and triplets.

#### 3a. N\textsubscript{3}\textsuperscript{+}. The formation of the X\Sigma\textsuperscript{−} state of the N\textsubscript{3}\textsuperscript{+} cation is succinctly described by Scheme 6. Our results (\(D_e\) and \(r_e\)) are in agreement with experimental values; notice in particular (Table 2) the (Mulliken) charge decrease on the “terminal” nitrogen, from +1 to +0.29 because of the “dative” bond character. Figure 1 shows the potential energy curve (PEC), i.e., a “slice” through the corresponding potential energy surface, of the process N\textsubscript{3}\textsuperscript{+}(P) + N\textsubscript{2}(XY\Sigma\textsuperscript{+}) → N\textsubscript{3}\textsuperscript{+}(X\Sigma\textsuperscript{−}) at the CCSD(T) level. A similar PEC is presented through the singlet surface of the N\textsubscript{3}\textsuperscript{+} a\Delta\textsubscript{1} state, whose bonding nature is described in Scheme 7a, and correlating to N\textsubscript{3}\textsuperscript{+}(D) + N\textsubscript{2}(XY\Sigma\textsuperscript{+}). With respect to these fragments (minimal energy path), \(D_e\) = 98.3 kcal/mol at \(r_e\) = 1.189 Å (Table 2).

#### 3b. NCO\textsuperscript{+}. We could imagine that, at equilibrium, the bonding in the X\Sigma\textsuperscript{−} state of NCO\textsuperscript{+} is formed in a similar fashion as in N\textsubscript{3}\textsuperscript{+}, Scheme 6. However, because IE[N(4S)] > IE[CO(X\Sigma\textsuperscript{+})], Table 1, what really happens is described by the following vbL icon, that is, the adiabatic products are...
TABLE 2: Total Energies $E$ (hartree), Bond Energies $D_{ij}$ (kcal/mol), Geometries $r_{ij}$ (Å), Mulliken Charges on Nitrogen ($q_{N}$), and Singlet–Triplet Separations $\Delta E$ (eV) of the Species $X N Y^+ / N R^+$ ($X Y = N_2, CO$ and $R = He, Ne, Ar, and Kr) and $NNH_3^+$ at RCCSD(T)/cc-pVTZ Level of Theory (Experimental Values in Parentheses)

<table>
<thead>
<tr>
<th>species</th>
<th>$-E$</th>
<th>$D_{ij}(N^+/XY/R)^{b}$</th>
<th>$D_{ij}(N+XY^+/R)^{c}$</th>
<th>$e_{ij}(N−X/−R)$</th>
<th>$r_{ij}(X−Y)$</th>
<th>$q_{N}{d}$</th>
<th>$\Delta E(S−T)$</th>
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</thead>
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<tr>
<td>$N_2^+(\tilde{X}\Sigma_g^+)^{a}$</td>
<td>163.48852</td>
<td>81.9 (81.4)$^{a}$</td>
<td>104.9</td>
<td>1.192 (1.193)$^{a}$</td>
<td>1.192 (1.193)$^{a}$</td>
<td>+0.29</td>
<td>1.393 (1.13)$^{a}$</td>
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<tr>
<td>$N_2^+(\tilde{a}\Pi _g)^{a}$</td>
<td>163.3734</td>
<td>98.3</td>
<td>136.1</td>
<td>1.189</td>
<td>1.189</td>
<td>+0.2</td>
<td>1.36</td>
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<tr>
<td>$NCO^+(\tilde{X}\Sigma^−)$</td>
<td>167.32628</td>
<td>117.1</td>
<td>104.8</td>
<td>1.359</td>
<td>1.130</td>
<td>+0.23</td>
<td>1.476</td>
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<td>$NCO^+(\tilde{a}\Delta)$</td>
<td>167.27205</td>
<td>131.6</td>
<td>134.0</td>
<td>1.300</td>
<td>1.153</td>
<td>+0.29</td>
<td>1.36</td>
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<td>$NCO^+(\tilde{X}\Pi )$</td>
<td>110.71288</td>
<td>172.1</td>
<td>58.5</td>
<td>1.455$^{a}$</td>
<td>1.030$^{a}$</td>
<td>+0.15</td>
<td>1.984</td>
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<td>$NCO^+(\tilde{a}\Pi _i)$</td>
<td>110.63997</td>
<td>174.9</td>
<td>76.0</td>
<td>1.436$^{a}$</td>
<td>1.032$^{a}$</td>
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<td>$NHe^+(\tilde{X}\Pi )$</td>
<td>56.89178</td>
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<td>$NHe^+(\tilde{a}\Pi )$</td>
<td>56.81399</td>
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<td>252.0</td>
<td>1.539</td>
<td>+0.86</td>
<td>2.117</td>
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<td>$NNe^+(\tilde{X}\Sigma^−)$</td>
<td>182.80128</td>
<td>9.27</td>
<td>167.8</td>
<td>1.769</td>
<td>+0.88</td>
<td>2.122</td>
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<td>$NNe^+(\tilde{a}\Pi )$</td>
<td>182.72330</td>
<td>8.85</td>
<td>182.1</td>
<td>1.762</td>
<td>+0.87</td>
<td>2.117</td>
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<tr>
<td>$NAr^+(\tilde{X}\Pi )$</td>
<td>581.10613</td>
<td>49.6</td>
<td>75.4</td>
<td>1.837</td>
<td>+0.50</td>
<td>2.037</td>
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<td>$NAr^+(\tilde{a}\Pi )$</td>
<td>581.03127</td>
<td>51.1</td>
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<td>1.805</td>
<td>+0.45</td>
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<td>$NN\text{Kr}^+(\tilde{X}\Sigma^−)$</td>
<td>2806.33679</td>
<td>67.6</td>
<td>55.9</td>
<td>1.945</td>
<td>+0.37</td>
<td>1.977</td>
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<tr>
<td>$NN\text{Kr}^+(\tilde{a}\Pi )$</td>
<td>2806.26412</td>
<td>70.5</td>
<td>73.6</td>
<td>1.897</td>
<td>+0.30</td>
<td>1.977</td>
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$^a$ Calculated at $D_{ij}$ symmetry. $^b$ Dissociation with respect to $N^+(P)$ for triplets and to $N^+(D)$ for singlets ($XY/R = ground-state singlet$). $^c$ Dissociation with respect to $N(S)$ for triplets and to $N(D)$ for singlets ($XY/R^+ = ground state doublet$). $^d$ Mulliken charges on the terminal N at the Hartree–Fock level. $^e$ Experimental value ($D_{ij}$) from ref 29. $^f$ Experimental value ($r_{ij}$) from ref 17. $^g$ Experimental value from ref 29; at the MRCI/cc-pVQZ level, Rosmus et al. (ref 30) obtained $\Delta E(S−T) = 1.30$ eV. $^h$ The N−NH$_3$ distance. $^i$ The NNH$_2$−H distance, $\angle$NH$_3$ and $\angle$NNH angles $\approx$ 109.6$^\circ$ and 109.3$^\circ$ ($\tilde{A}_2$), 110.0$^\circ$ and 108.9$^\circ$ ($\tilde{A}_1$).

Figure 1. Potential energy profiles of the processes $N_2^+(\tilde{X}\Sigma_g^+) \rightarrow N_2^+(\tilde{P}; M = 0) + N_2(\tilde{X}\Sigma_g^+)$ and $N_2^+(\tilde{a}\Pi _g) \rightarrow N_2^+(\tilde{D}; M = \pm 2) + N_2(\tilde{X}\Sigma_g^+)$ at the RCCSD(T)/cc-pVTZ level.

N($S^+$) + CO($X^2\Sigma^+$). Scheme 10 suggests that the $-\text{C}O$ moiety remains practically intact upon bonding and that the complete N−CO CEC cannot be constructed at the RCCSD(T) level because of the covalent character of the N−CO bond. This is exactly what happens: Figure 2 shows the N−CO+$^+$ PEC around equilibrium, whereas the NC−O bond length is predicted to be 1.130 Å as compared to 1.123 Å of CO($X^2\Sigma^+$), Tables 2 and 1. $D_{ij}(N−CO^+)$ = 104.8 kcal/mol with respect to N($S^+$) + CO($X^2\Sigma^+$).

The situation is different however for the $\tilde{a}\Delta$ state of NCO$^+$, approximately 1.5 eV above its $X^2\Sigma^+$ state. Whether the reaction

NCO$^+(\tilde{a}\Delta) \rightarrow N^+(\tilde{D}) + CO(X^1\Sigma^+)$

or

NCO$^+(\tilde{a}\Delta) \rightarrow N^+(\tilde{D}) + CO^+(X^2\Sigma^+)$

occurs, it depends on the process N($S^+$) + e$^−$ → N$^+(P)$ → N$^+(D)$ vs N($S^+$) + CO($X^2\Sigma^+$) → N$^+(D)$ + CO$^+(X^2\Sigma^+)$ + e$^−$. Experimentally, the first one requires 16.428 eV vs 16.398 eV of the second, whereas calculationally, the corresponding values are 16.533 vs 16.638 eV, respectively (Table 1). Indeed, according to our calculations, NCO$^+(\tilde{a}\Delta)$ correlates to N$^+(\tilde{D})$ + CO($X^2\Sigma^+$); thus, a full PEC could be constructed at the RCCSD(T) level, Figure 2, because of the dative character of the N−CO(\tilde{a}\Delta) bond, similar to that of Scheme 6. The N−CO+$^+$ $D_{ij}$ is 131.6 kcal/mol with respect to N$^+(\tilde{D})$ + CO($X^2\Sigma^+$) or 134.0 kcal/mol with respect to N$^+(\tilde{D})$ + CO$^+(X^2\Sigma^+)$, a 2.4 kcal/mol difference equal to the difference 16.638 − 16.533 = 0.105 eV reported above.

3c. $NNH_3^+$. The previous bonding scenario can be repeated here; according to Table 2, the least energy paths because of the much higher IE of N($S^+$) vs NH$_3$ are $NNH_3^+(\tilde{X}\tilde{A}_2) \rightarrow N^+(S)$. 

Figure 2. Potential energy profile of the process NCO$^+(\tilde{a}\Delta) \rightarrow N^+(D; M = \pm 2) + CO(X^1\Sigma^+)$ and part of the corresponding curve NCO$^+(X^2\Sigma^+) \rightarrow N(S^+) + CO^+(X^2\Sigma^+)$; see text. RCCSD(T)/cc-pVTZ level.
TABLE 3: Total Energies \( E \) (hartree), Bond Dissociation Energies \( D_e \) (kcal/mol), Geometries \( r_a \) (Å), \( \theta_e \) (Degrees), and Mulliken Charges on the Central Nitrogen \( q_m \) of the \( ^1A_1 \) State of N(XY)\( _2^2 \)/NR\( _2^+ \) (XY = N\( _2 \), CO and R = He, Ne, Ar, and Kr) and N(NH\( _3 \))\( _2^2 \)(\( ^1A_1 \)) Molecular Systems at the RCCSD(T)/cc-pVTZ Level

<table>
<thead>
<tr>
<th>System</th>
<th>( -E )</th>
<th>( N^1(\text{D})^e )</th>
<th>( N^0(\text{D})^e )</th>
<th>( N^1(\text{D})^e )</th>
<th>( N^0(\text{D})^e )</th>
<th>( D_e ) (kcal/mol)</th>
<th>( r_e(\text{NR}/\text{R}) )</th>
<th>( r_e(X-Y) )</th>
<th>( \theta_e ) (XNX/RNR)</th>
<th>( \theta_e ) (NXY)</th>
<th>( q_m )</th>
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</thead>
<tbody>
<tr>
<td>N(N( _2 ))( _2^+ )</td>
<td>272.88521</td>
<td>277.6</td>
<td>96.2</td>
<td>119.2</td>
<td>13.23</td>
<td>1.116</td>
<td>108.6</td>
<td>167.3</td>
<td>-0.10</td>
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<td></td>
</tr>
<tr>
<td>N(CO( _2 ))( _2^+ )</td>
<td>280.65644</td>
<td>277.6</td>
<td>96.2</td>
<td>119.2</td>
<td>13.23</td>
<td>1.116</td>
<td>108.6</td>
<td>167.3</td>
<td>-0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(N( _2 ))( _2^+ )</td>
<td>167.24857</td>
<td>199.6</td>
<td>97.7</td>
<td>1.466</td>
<td>f</td>
<td>105.2</td>
<td>f</td>
<td>-0.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(N( _2 ))( _2^+ )</td>
<td>59.71693</td>
<td>242.6</td>
<td>190.3</td>
<td>1.762</td>
<td>180.0</td>
<td>0.86</td>
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<tr>
<td>N(N( _2 ))( _2^+ )</td>
<td>1108.10028</td>
<td>108.0</td>
<td>18.9</td>
<td>44.7</td>
<td>1.937</td>
<td>104.2</td>
<td>0.25</td>
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<tr>
<td>N(N( _2 ))( _2^+ )</td>
<td>5558.5489</td>
<td>45.1</td>
<td>33.4</td>
<td>2.034</td>
<td>107.0</td>
<td>0.05</td>
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<tr>
<td>N(N( _2 ))( _2^+ )</td>
<td>272.95934</td>
<td>148.6</td>
<td>185.7</td>
<td>99.4</td>
<td>123.8</td>
<td>1.318</td>
<td>1.112</td>
<td>108.9</td>
<td>167.3</td>
<td>-0.02</td>
<td></td>
</tr>
<tr>
<td>N(CO( _2 ))( _2^+ )</td>
<td>280.73596</td>
<td>280.73596</td>
<td>275.2</td>
<td>144.7</td>
<td>123.8</td>
<td>1.318</td>
<td>1.112</td>
<td>108.9</td>
<td>167.3</td>
<td>-0.02</td>
<td></td>
</tr>
</tbody>
</table>

\( ^1A_1 \) to \( ^2A_2 \) complex, see Scheme 12.

+ NH\( _4 ^+ \)(\( \bar{X}^2A''_2 \)) and NNH\( _5 ^+ \)(\( \bar{A} \)) \( \rightarrow \) N\( ^1(\text{D})^e \) + NNH\( _5 ^+ \)(\( \bar{X}^2A''_2 \)) with \( D_e = 58.5 \) and 76.0 kcal/mol, respectively. In the singlet state and at the equilibrium, we could think that the bonding is of dative character of the NH\( _4 ^+ \) lone pair to the N\( ^1(\text{D})^e \) state with a bonding energy of around N(N\( _2 \))\( _2^+ \) (\( ^1A_1 \)) of 174.9 kcal/mol. The neutralization of the terminal nitrogen from the processes N\( ^0(\text{D})^e \) + 2NH\( _3 ^+ \)(\( \bar{X}^2A''_2 \)) as pictured in Scheme 7b. It is also of interest to follow the evolution of Mulliken Hartree–Fock charges of the three distinct nitrogen (N\( _e \), N\( f \), and N\( g \), see Scheme 1), along the reaction path in the inset of Figure 3, subject to the charge conservation condition \( q_m(r) \) + 2\( q_m(r) \) = +1. The central nitrogen (N\( _e \)) starts with -0.10 \( e \) at equilibrium (see also Table 3) and increases in a sigmoid fashion to +1.8 at infinity. At equilibrium, N\( \beta \) carries a +0.36 \( e \) charge, diminishes to zero around 2.2 \( A \), acquires a slight negative charge further apart by induction, and eventually approaches zero. The terminal N\( \gamma \) begins at +0.19 and drops to zero at infinity, slowly and almost linearly. Note also that the N\( \alpha \) to N\( \beta \) balance, \( r_e = 1.116 \) \( A \) (Table 3) is equal to the average of the N\( _2 (X^2 \Sigma^+ \_g^\prime) \) and N\( _2 (X^2 \Sigma^+ \_g) \) bond lengths, (1.104 + 1.123)/2 = 1.114 \( A \), Table 1.

We believe that the above discussion leaves no doubt as to the bonding nature of N\( _2 ^+ (\bar{X}^2A''_2) \), i.e., of two dative (harpoon-like) bonds “titrating” the N\( ^1(\text{D})^e \) atom, Scheme 7b. Instead of writing an ever-increasing number of resonance structures of obscure origin, the simplest and most accurate way to describe the bonding in N\( _2 ^+ \) in a chemical symbolic language would be

\[ \text{N=N=N} \]

by pulling apart the two end \( \text{N}_2 \) fragments, starting from the equilibrium geometry and maintaining the \( \text{C}_2 \) symmetry, while minimizing at the same time the N–N distance of the two terminal \( \text{N}_2 \) fragments. The asymptotic products are N\( ^1(\text{D})^e \) + 2NH\( _3 ^+ \)(\( \bar{X}^2A''_2 \)) as pictured in Scheme 7b. It is also of interest to follow the evolution of Mulliken Hartree–Fock charges of the three distinct nitrogen (N\( _e \), N\( f \), and N\( g \), see Scheme 1), along the reaction path in the inset of Figure 3, subject to the charge conservation condition \( q_m(r) \) + 2\( q_m(r) \) = +1. The central nitrogen (N\( _e \)) starts with -0.10 \( e \) at equilibrium (see also Table 3) and increases in a sigmoid fashion to +1.8 at infinity. At equilibrium, N\( \beta \) carries a +0.36 \( e \) charge, diminishes to zero around 2.2 \( A \), acquires a slight negative charge further apart by induction, and eventually approaches zero. The terminal N\( \gamma \) begins at +0.19 and drops to zero at infinity, slowly and almost linearly. Note also that the N\( \alpha \) to N\( \beta \) balance, \( r_e = 1.116 \) \( A \) (Table 3) is equal to the average of the N\( _2 (X^2 \Sigma^+ \_g^\prime) \) and N\( _2 (X^2 \Sigma^+ \_g) \) bond lengths, (1.104 + 1.123)/2 = 1.114 \( A \), Table 1.

We believe that the above discussion leaves no doubt as to the bonding nature of N\( _2 ^+ (\bar{X}^2A''_2) \), i.e., of two dative (harpoon-like) bonds “titrating” the N\( ^1(\text{D})^e \) atom, Scheme 7b. Instead of writing an ever-increasing number of resonance structures of obscure origin, the simplest and most accurate way to describe the bonding in N\( _2 ^+ \) in a chemical symbolic language would be

\[ \text{N=N=N} \]

with the understanding that the in situ central nitrogen carries the memory of a N\( ^1 \) D state.

At the RCCSD(T)/cc-pVQZ level, \( D_e = 98.3 \) kcal/mol for the process N\( _2 ^+ (\bar{A} \bar{A}_g) \rightarrow N^0(\text{D})^e + N_2 (X^2 \Sigma^+ \_g) \), Table 2. From Table 3, we see that the breaking of two \( \text{N}_2 \) bonds requires 144.7 kcal/mol; therefore, the \( D_e \) for the removal of one \( \text{N}_2 (X^2 \Sigma^+ \_g) \) from N\( _2 ^+ \) amounts to 144.7 - 98.3 = 46.4 kcal/mol. Finally, a large (40.6 kcal/mol) inversion barrier accompanied by a significant decrease of the N\( _2 \)--N\( \gamma \) distance at linearity (N\( \beta \)--N\( _e \), 2.120 \( A \); N\( \gamma \)--N\( \beta \), 1.129 \( A \)) is calculated for N\( _2 ^+ \) at the same level of theory.

3f. N(CO\( _2 \))\( _2^+ \). The above discussion for the N\( _2 ^+ \) molecule holds also for the N(CO\( _2 \))\( _2^+ \)(\( \bar{X}^2A''_2 \)) species. From Table 3, it is

\[ \text{N=N=N} \]
seen that the nitrogen atom carries a negative charge of 0.1 e\textsuperscript{−} at the Hartree–Fock/cc-pVTZ level, where the NC\textsubscript{O} bond distance is very similar to that of the free CO(X \textsuperscript{1}Σ\textsuperscript{+}) or CO\textsuperscript{+}(X \textsuperscript{2}Σ\textsuperscript{+}), Table 1, and in the light of section 3b (NCO\textsuperscript{+}), we are rather certain that the bonding is similar to that of N(N\textsubscript{2})\textsubscript{2}\textsuperscript{+}, Scheme 7b, i.e. with the in situ N\textsuperscript{+} in the \textsuperscript{1}D state. A similar potential energy diagram to that of N(N\textsubscript{2})\textsubscript{2}\textsuperscript{+} (Figure 3) is shown in Figure 4. The two CO molecules are pulled away in a symmetrical fashion while optimizing at the same time the C–O distance. In the inset, we observe the (HF) charge evolution for the three unique atoms, essentially identical to that of N(N\textsubscript{2})\textsubscript{2}\textsuperscript{+}. What is remarkable is the very high \(D_e\) value for the process N(CO)\textsubscript{2}\textsuperscript{+}(X \textsuperscript{1}Σ\textsuperscript{+}) \(\rightarrow\) N\textsuperscript{+}(\textsuperscript{1}D) + 2CO(X \textsuperscript{1}Σ\textsuperscript{+}), \(D_e = 275.2\) kcal/mol (Table 3), twice as large of the N(N\textsubscript{2})\textsubscript{2}\textsuperscript{+} corresponding value. This could be attributed to the availability of the σ lone pair of electrons residing on the carbon atom (:C=O), thus rendering the dative mechanism more efficient. Knowing the \(D_e\) value for the reaction NCO\textsuperscript{+}(\textsuperscript{a}1\Delta) \(\rightarrow\) N\textsuperscript{+}(\textsuperscript{1}D) + CO(X \textsuperscript{1}Σ\textsuperscript{+}) to be 131.6 kcal/mol (Table 2), the \(D_e\) for abstracting one CO(X \textsuperscript{1}Σ\textsuperscript{+}) from N(CO)\textsubscript{2}\textsuperscript{+} is 275.2 – 131.6 = 143.6 kcal/mol at the triple-\(\tilde{\alpha}\) level. At the same level of theory, we find that N(CO)\textsubscript{2}\textsuperscript{+} is rather floppy; the barrier to linearity (N–C, 1.233 Å; C–O, 1.138 Å) is calculated to be 3.0 kcal/mol, in accord with previous calculations.\textsuperscript{2,31}
3g. N(NH₃)₂⁺. When the geometry of the N(NH₃)₂⁺ molecule is minimized at the RCCSD(T)/cc-pVTZ level under C₂ᵥ symmetry, the following structure is obtained. Interestingly enough, the ∠NNN angle is practically the same as the corresponding angle of the N(N₂)₂⁺ system. Notice the very large negative Mulliken-HF charge on the central nitrogen, −0.38 e⁻. From Tables 2 and 3, we deduce that the $D_s = 76.0 \text{ kcal/mol}$ for the process NNH₃⁺ (a1A₁) → N(D) + NH₃⁺ (X₂A₂⁺), thereby the second NH₃ molecule enters with a binding energy of 161.0 − 76.0 = 85.0 kcal/mol. Or, using pictures:

Of course, the two N–N bonds are equivalent.

To the best of our knowledge, neither experimental nor theoretical results exist in the literature concerning the N(NH₃)₂⁺ cation. What is of interest from an experimental point of view, however, is that the 1 A₁ N(NH₃)₂ + species according to the energy diagram of Figure 5 is isolable at the RCCSD(T)/cc-pVTZ level. The wiggly line represents the level of the electrostatic interaction N(NH₃)⁺...NH₃; $e$: assuming that $e$ is smaller than 39 kcal/mol, a reasonable hypothesis, N(NH₃)₂⁺ (1A₁) is the ground state. We would like to mention at this point that the homologous species N(PhH)₂⁺ and P(PhH)₂⁺, where Ph = phenyl group (C₆H₅), have been isolated.²²

3h. NR₂⁺; R = He, Ne, Ar, and Kr. When Scheme 11 is followed for the NR⁺ (a’Δ) series, a second R atom can be inserted in the available p (pₓ) orbital of the in situ N⁺ (1D) atom, resulting in the NR₂⁺ singlet series of molecules. Table 3 reports atomization energies with respect to different channels, along with structural parameters at the RCCSD(T)/cc-pVTZ level of theory. From Table 3, we observe the stark difference between the atomization energies of the two pairs of molecules NH₂⁺, NNe₂⁺ and NAr₂⁺, NKr₂⁺. The differences are 5.95, 12.5 and 67.4, 93.6 kcal/mol, respectively. In addition, the first two species are linear (∠RNRR = 180°), whereas the other two are strongly bent and with similar ∠RNRR angles, similar also to the ∠N₂N₂N₂ of N₂⁺. The atomization energies of the NR₂⁺ series increase almost linearly with the polarizabilities of the R atoms (0.204456, 0.3946, 1.646, and 2.48 Å³ for He, Ne, Ar, and Kr, respectively) and inversely proportional to their electron-donor ability, i.e., to their IE values (Table 1). This is also evident from the charge on the N atom that decreases dramatically from He to Kr (Table 3).

Quite interestingly, the atomization energy of NHe₂⁺ with respect to N⁺ (1D) + 2He(S), 5.95 kcal/mol, is nearly equal to the atomization energy of LiHe₂(A₂B₁) with respect to Li(2P) + 2He(S), 5.57 kcal/mol.³⁴ The latter molecule is bent but extremely floppy having an inversion barrier of 32 cm⁻¹;³⁴ on the other hand NHe₂⁺ is linear but also floppy: bending NHe₂⁺ from 180° to 120° requires 1.83 kcal/mol, at the RCCSD(T)/cc-pVTZ level.

The NNe₂⁺ species is also linear, with an atomization energy of 12.5 kcal/mol with respect to N⁺ (1D) + 2Ne(S), and equally floppy, with NHe₂⁺ requiring 1.66 kcal/mol to become bent at 120°.

The picture changes when we move to the NAr₂⁺ and NKr₂⁺ species: although the binding process is the same, i.e., two dative bonds, the atomization energies change drastically because of much larger polarizabilities and much smaller IEs of Ar and Kr as compared to He and Ne. As a result, atomization energies as large as 93.6 kcal/mol are calculated for NKr₂⁺ at severely bent geometries and with respect to N⁺ (1D) + 2R(F; Ar, Kr). In addition, NAr₂⁺ (a¹A₁) and NKr₂⁺ (a¹A₁) are bound with respect to N⁺ (2P) + 2Ar and N⁺ (2S) + Kr + + Kr by 18.9 and 33.4 kcal/mol, respectively. Figure 6 shows the energy separation ($T_e$) between the NR₂⁺ (singlets) and NR⁺ + R (triplets). The energy differences shown should be increased by the electrostatic interactions, NR⁺ (Σ⁺) + R, not larger than 5 – 6 kcal/mol for the Kr, and much smaller for the He atom (for instance, the electrostatic binding energy of LiKr⁺ (X’Σ⁺) is 9.0 kcal/mol).
4. Synopsis

For the series of molecules N(N2)2⁺, N(CO)2⁺, N(NH3)2⁺, and NR2⁺, where x = 1, 2 and R = He, Ne, Ar, and Kr, we have obtained structural parameters and bonding energetics using RCCSD(T) methods coupled with triple and quadruple-ζ correlation-consistent basis sets. The motivation of the present work was to elucidate the bonding nature, mainly of N5⁺ and N(CO)2⁺, two recently isolated species. We argue that the much used resonance concept for explaining the bonding of N5⁺ is of no use, as a matter of fact is misleading, and that the bonding can be understood by using calculable properties. Obviously, molecules are formed by atoms in well-defined stationary states, ground or otherwise.

All of the above, seemingly unrelated molecular systems (x = 2), can be easily understood by realizing that the in situ central nitrogen N⁺ finds itself in the first excited 1D state, forming two dative (harpoon-like) bonds originating from the two substituents.

For the systems N(N2)2⁺ and N(CO)2⁺, our calculated structural parameters at the quadruple-ζ level are the best so far reported in the literature; in addition, and for the first time, we report singlet potential energy curves of the processes N(XY)2⁺ → N⁺(1D) + 2XY, where XY = N2(XΣ⁺), CO(XΣ⁺). The binding energies with respect to the ground states NXY⁺(XΣ⁺) + XY(XΣ⁺) are 14.3 and 109.6 kcal/mol for XY = N₂ and CO, respectively. This means that the N(CO)2⁺ system is much more stable than N5⁺, as indeed has been proven experimentally. Of course, resonance structures of N(CO)2⁺ similar to those of N(N2)2⁺ do not support, explain, or predict the much larger stability of N(CO)2⁺ vs N(N2)2⁺.

Within the same spirit, our study has been extended to the systems N(NH3)2⁺ and NR2⁺, R = He, Ne, Ar, and Kr, where writing resonance structures is rather far-fetched. Nevertheless, the N(NH3)2⁺ singlet state is clearly isolable according to our results, whereas very large binding energies are observed for the NAr₂⁺ and NKr₂⁺ systems. As a matter of fact the NKr₂⁺ cation could be even isolable, with the singlet state being a little bit more than 23 kcal/mol above the global electrostatic NKr⁺····Kr triplet minimum. Although we do not have any numerical data for the Nxe₂⁺ molecule, it is rather obvious that this system could be also isolable if combined with an appropriate counterion.

Acknowledgment. This work was supported by the National and Kapodistrian University of Athens through Grant No. 70/4/3340. One of us (I.S.K.K.) expresses his gratitude to the Hellenic State Scholarships Foundation (IKY) for financial support. The generous computing time from the National Center for Scientific Research, DEMOKRITOS, is greatly appreciated.

References and Notes


(22) Occam’s razor maxim says: Pluralitas non est ponenda sine necessitate; that is, “multiplicity ought not to be posited without necessity”, see, for example, Encyclopædia Britannica 1971; vol. 16, p 858.

(23) Unpublished results of this laboratory.


