Theoretical Survey of the Potential Energy Surface of Ethylenediamine + Cu^+ Reactions

Manuel Alcamí,* Alberto Luna, Otilia Mó, and Manuel Yáñez

Departamento de Química, C-9, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

Jeanine Tortajada

Laboratoire Analyze et Environnement, UMR CNRS 8587, Université d'Evry Val d'Essonne, Institut des Sciences, Boulevard François Mitterrand, 91025 Evry Cedex, France

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Density functional theory (DFT) calculations have been carried out to explore the potential energy surface (PES) associated with the gas-phase reactions between ethylenediamine (**En**) and Cu^+. The structures and bonding characteristics of the different stationary points of this PES have been investigated at the B3LYP/6-311G(d,p) level. Final energies were obtained by means of B3LYP/6-311+G(2df,2p) single point calculations. **En** strongly binds Cu^+ by forming a chelated structure in which the metal cation binds to both amino groups. Different mechanisms leading to the loss of H_2, NH_3, and CuH are analyzed in terms of the topology of the PES. The most favorable mechanism corresponds to the loss of H_2, through a process in which the transition metal cation acts as a carrier, connecting a hydrogen atom from a methylene group with a hydrogen atom of one of the amino groups. The product ion is a five-membered ring in which Cu^+ bridges between N atoms of the $H_2N-CH_2-CH-NH$ moiety. The loss of ammonia is less favorable, because all mechanisms involve higher activation barriers. The most favorable of these mechanisms implies hydrogen shift between the two methylene groups that triggers a spontaneous hydrogen shift between the two amino groups, favored by the existence of a strong intramolecular hydrogen bond. These mechanisms explain the experimental results involving fully C-deuterated species, where only a loss of HD and NH_3 are observed. The loss of HCu is also discussed.

1. Introduction

One important objective in modern chemistry is the design of bidentate or multidentate bases able to form very stable chelates with metals and metal ions. The ultimate goal, as far as environmental chemistry is concerned, is to obtain bases able to bind toxic metals, or toxic metal ions more strongly than water, or other natural compounds found in the soil. This requires unavoidably a good knowledge on the bonding within these chelated structures, and also importantly, a good knowledge on the way the complexes formed decompose in unimolecular processes. The first approach to the problem can be done in combined theory−experiment studies in the gas phase that have the advantage of providing information on the intrinsic reactivity of the system, without interference from the medium. This motivated a great deal of attention in the past few years as it is well reflected in several reviews,[1−5] and many papers dealing with the reactivity of metal cations with typical bidentate bases, such as dimethyl ether, dimethoxyethane, polyethers, glycolic acid, or glycerol, have been reported in the literature.[6−10] Also, many studies have been devoted to discussing the formation of metal complexes of ethylenediamine (**En**) in solution,[11−14] because **En** is one of the most widely used metal ligands, and its derivatives are also good chelating agents or good precursors for the synthesis of new ones.[15] Surprisingly, similar studies considering the structure and energy of **En**−metal complexes in the gas phase are scarce,[16] and the first experimental results of the gas-phase reactions between (**En**) and Cu^+ have been published very recently.[17] In this publication, only a summary of the possible mechanisms involved in the **En** + Cu^+ reactions are proposed. The aim of the present paper is to offer a complete survey of the potential energy surface, carried out through the use of density functional theory (DFT) methods that may contribute to a rationalization of the experimental results.

2. Computational Details

Standard density functional theory (DFT) calculations have been carried out by means of the Gaussian-98 suites of programs.[18] Among the different functionals available in this program package we have chosen the B3LYP approach, because it has been shown[19,20] to provide both geometries and vibrational frequencies in fairly good agreement with experiment. On the other hand, the B3LYP approach presents few instabilities and for the particular case of Cu^+ complexes is free of the pathologies that affect high-level ab initio formalisms, as the G2 theory or even the CCSD(T) methods are used.[21−23]

The geometries of the different species under consideration have been optimized by using the hybrid B3LYP functional, in conjunction with the all electron (14s9p5d/9s5p3d) basis of Wachters−Hay for Cu[24,25] supplemented with one set of f polarization function, and the 6-311G(d,p) basis set for the remaining atoms of the system. This B3LYP approach combines Becke's three-parameter nonlocal hybrid exchange potential[26] with the nonlocal correlation functional of Lee, Yang, and Parr.[27] The harmonic vibrational frequencies of the different stationary points of the PES have been calculated at the same level of

* Corresponding author. E-mail: manuel.alcami@uam.es.

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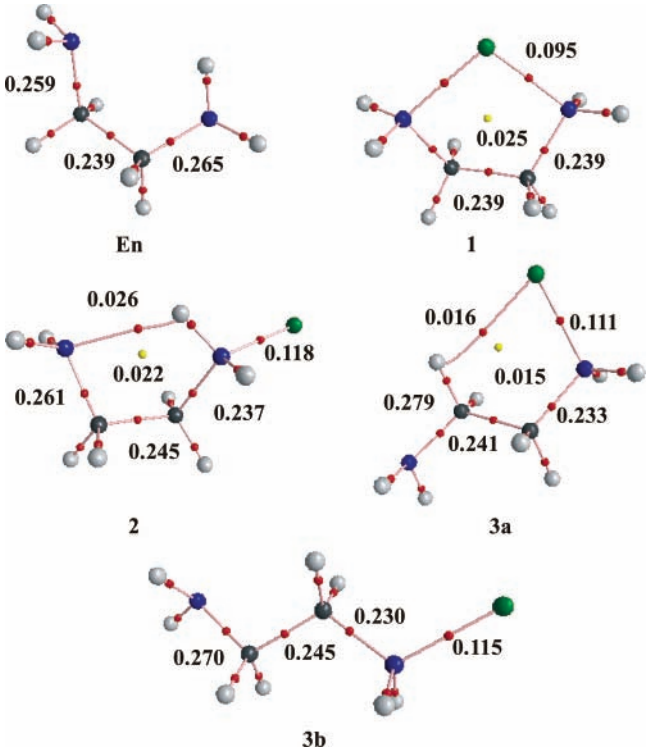

Figure 1. Molecular graphs for ethylenediamine and ethylenediamine−Cu^+ adducts, showing the position and electron density at relevant bcps (red) and ring critical points (yellow). All values are in e au^{-3}.

theory to estimate the corresponding zero point energies (ZPE) and to classify the stationary points of the PES as local minima or transition states (TS).

Final energies have been obtained using the (14s9p5d/9s5p3d) Wachter−Hay's basis, supplemented with a set of (1s2p1d) diffuse components and with two sets of f functions and one set of g functions as the polarization basis for Cu combined a 6-311+G(2df,2p) basis set for first-row atoms. It has been shown[21,28] for some smaller Cu^+ complexes that the binding energies obtained at this level, which hereafter and for the sake of conciseness we will name as B3LYP/6-311+G(2df,2p), are quite reliable.

We have also made use of the atoms in molecules (AIM) theory of Bader to characterize the bonds and the characteristics of the interactions inside the different complexes. These calculations have been performed by using the AIM2000 program package.[29]

3. Results and Discussion

Structure and Bonding of En−Cu^+ Complexes. The structure of **En** has been widely studied by both experimental and theoretical methods,[30−33] and therefore we shall concentrate our attention exclusively on the **En**−Cu^+ adducts.

The most stable adduct corresponds to a complex (**1**) in which the weak intramolecular N−H···N hydrogen bond that stabilizes **En** is replaced by a N−Cu^+−N bridge. An examination of the molecular graphs obtained by using the AIM theory for **En** and complex **1** (see Figure 1) indicates that the intramolecular hydrogen bond (IHB) in the former is so weak that no bond critical point (bcp) could be found associated with this interaction. Consistently, the calculated N−H harmonic vibrational frequencies for **En** appear as symmetric and asymmetric combinations, not only for the amino group acting as HB acceptor but also for that behaving as the HB donor. The formation of complex **1** leads to a significant activation of both C−N bonds, as reflected by the decrease in the charge density at the bcp and by a red shifting of the C−N stretching frequencies by 113 cm^{-1}.

The association of Cu^+ to the NH proton donor group of **En** reinforces the N−H···N IHB and leads to a secondary minimum, **2**, 17.6 kcal mol^{-1} higher in energy. This strengthening of the N−H···N IHB, associated with the enhancement of the acidity of the NH group, is reflected in a shortening of the N····N distance, and in the existence of a bcp (see Figure 1) and in a significant red-shifting (222 cm^{-1}) of the donor N−H stretching frequency.

Two other local mimina (**3a** and **3b**; see Figure 1), which can be considered the result of the interaction of Cu^+ with the trans isomer of **En**, lie 24.1 and 23.3 kcal mol^{-1} above the global minimum. As shown in Figure 1, complex **3a** presents an agostic-type interaction between Cu^+ and one of the C−H bonds of the closest methylene group, similar to the other reported in the literature.[34−36]

The structures of the different local minima (species **4**−**17**) and transition states located in the PES will not be discussed in detail, but they will be schematized in the energy profiles of Figures 2−7 and are given as Supporting Information together with their corresponding total energies. We have also investigated the structures of the products originated by the most relevant losses (H_2, NH_3, HCu) detected in the mass spectra, that will be named, hereafter, as **P1(H_2)**, **P2(H_2)**, ..., **P1(NH_3)**, **P2(NH_3)**, ..., **P1(HCu)**, respectively.

Unimolecular Mechanisms Associated with En + Cu^+ Reactions. The MIKE spectrum of [**En**−^{63}Cu]$^+$ complexes reported in ref 17 shows three spontaneous losses corresponding to H_2, NH_3, and HCu, the first being the most important. In experiments using the C-tetradeuterated species, **En**-d_4, only the losses of HD, NH_3, and DCu are observed. In the following sections we shall present a systematic survey of the [**En**−Cu]$^+$ PES with the aim of finding the unimolecular mechanisms associated with the observed unimolecular fragmentations.

Loss of H_2. (a) Direct H_2 Loss from Adjacent XH_2 Groups. A first set of mechanisms that can be considered imply the direct loss of H_2 from two adjacent XH_2 groups through multicenter transition states similar to those proposed for alkane dehydrogenation reactions.[37]

In principle, three different mechanisms can be envisaged: the two hydrogen atoms coming (a) from two amino groups (denoted as NN mechanism), (b) from two methylene groups (denoted as CC mechanism), and (c) from one amino and one methylene group (denoted as NC mechanism). The corresponding energy profiles are presented in Figure 2. In all cases the reaction path leading to the corresponding minima has been calculated using the intrinsic reaction coordinate (IRC) method.

Even though the final products are quite stable, these three reaction mechanisms imply energy barriers that are not only too high (of the order of 100 kcal/mol), but more importantly, they are located above the **En** + Cu^+ entrance channel (see Figure 2). Under the experimental conditions it could be possible to have such activation by collisions with the residual gas, but it could explain only a small fraction of the observed products, and therefore these mechanisms cannot explain the dominant loss of H_2 observed experimentally.[17] Furthermore, only the CN mechanism would be consistent with the observed spectra for the C-tetradeuterated species, in which only the loss of HD is observed. Although the CN mechanism is the one with the smallest activation barrier of the three considered, the barrier

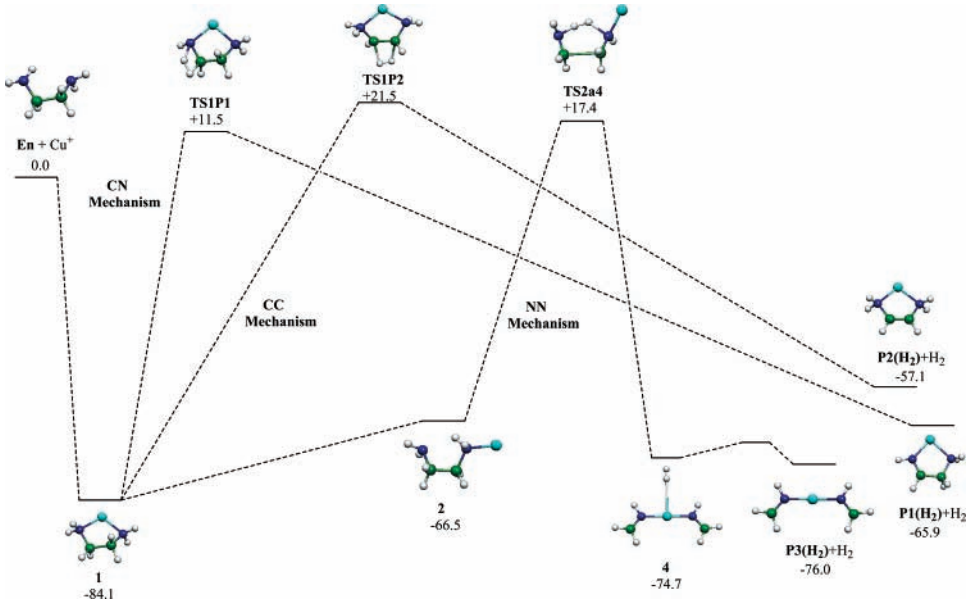

Figure 2. Energy profile for the reaction mechanisms corresponding to a direct loss of H_2 from adjacent XH_2 groups. Numbers refer to the relative stability (in kcal/mol) with respect to the **En** + Cu^+ entrance channel evaluated at the B3LYP/6-311+G(2df.2p)//B3LYP/6-311G(d,p) and including ZPE corrections. The dark blue circle denotes N atoms, green circles C atoms and light blue circles Cu atom.

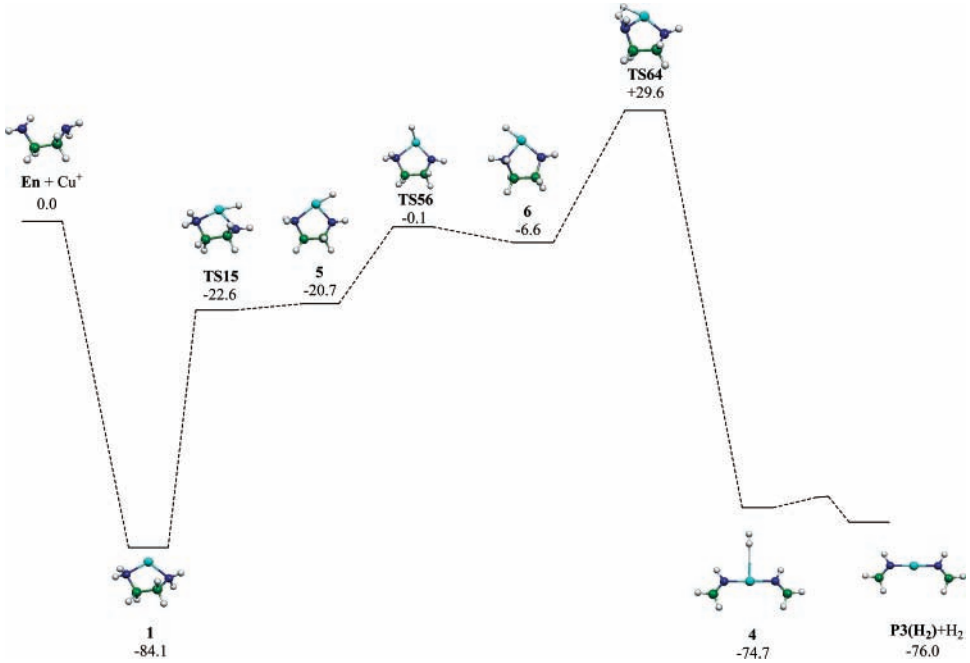

Figure 3. Energy profile for the "carrier" mechanism for the loss of H_2 in which the hydrogen atom comes from one of the amino groups. Energies and structures follow the same notation as in Figure 2.

is still much higher than the entrance channel and therefore this direct elimination of H_2 should not play a significant role.

(b) "Carrier" Mechanisms. Very often the transition metal cations act as "carriers" of hydrogen atoms in isomerization process. The fact that loss of CuH is also observed experimentally clearly indicates that in some of the intermediates of the reaction hydrogen atoms are attached to the metal, and therefore these intermediates can play some role in the observed loss of H_2. In principle, two different kinds of mechanisms of this type can be envisaged depending on if the H comes from an amino or from a methylene group. Let us consider first the case in which the hydrogen atom comes from one of the amino groups. This corresponds to the energy profile in Figure 3. Starting from **1**, structure **6** can be reached through the intermediate species **5**. In Figure 3 the transition state **TS15** is slightly lower in energy than local minimum **5**, when ZPE corrections are included. This is due to the fact that the reported energies are obtained from single point calculations with the larger 6-311+G(2df,2p) basis set at the optimized B3LYP/6-311G(d,p) geometries. Complex **6** evolves, through the interaction of the H attached to Cu with one of the hydrogens of the second amino group, to yield complex **4**, which eventually dissociates into **P3(H_2)** + H_2. However, the multicenter transition state (**TS64**), as the last step of the mechanism, implies an energy barrier too high (29.6 kcal/mol above the entrance channel) to be accessible under the experimental conditions.

Let us now consider an alternative "carrier" mechanism in which the H atom comes from a methylene group. The energy profile for such a mechanism is given in Figure 4. Starting from adduct **3a**, one can reach complex **7a** through the transition state

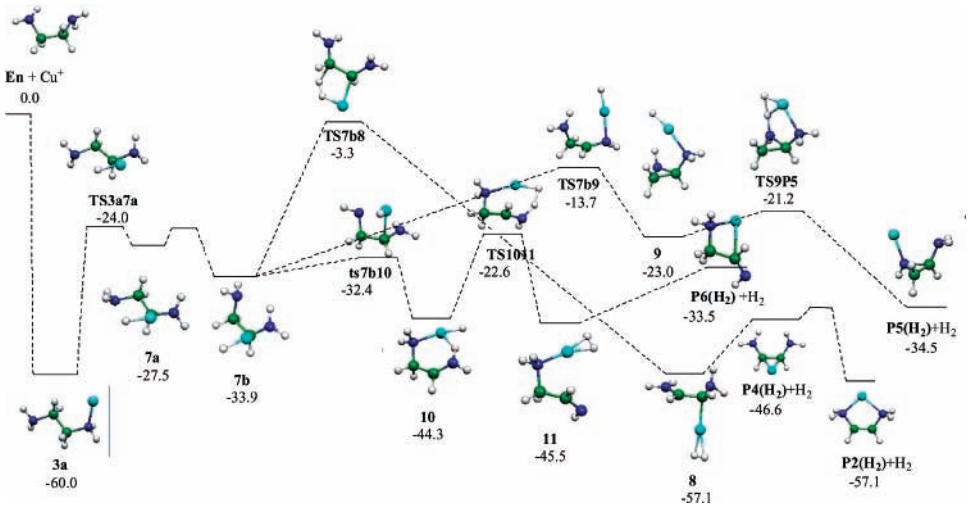

Figure 4. Energy profile for the "carrier" mechanisms for the loss of H_2 in which the hydrogen atom comes from one of the methylene groups. Energies and structures follow the same notation as in Figure 2.

TS3a7a. This hydrogen shift triggers a concomitant migration of the CuH (initially bonded to the nitrogen atom) toward the basic CH group formed after the H-shift. From this complex an internal rotation will lead to the more stable isomer **7b** (see Figure 4, note that all the internal rotations imply negligible energy barriers and have not been depicted in the figure).

Once structure **7b** is formed, three different mechanisms for the loss of H_2 can take place. As the hydrogen attached to Cu is close enough to the H atoms of the other methylene group (in complex **7b**, this distance is 2.865 Å), it is feasible to have a direct loss of H_2. This possibility involves the **TS7b8** transition state which lies 3.3 kcal/mol below the entrance channel. An IRC calculation indicates that this TS evolves to yield complex **8** (see Figure 4), which dissociates into **P4(H$_2$)** + H_2 without an activation barrier. From this complex an internal reorientation of Cu^+ would yield structure **P2(H$_2$)**.

A second mechanism implies the cyclization of **7b** by forming a new bond between the terminal amino group and the CH group and a concomitant migration of the CuH to the lone pair of the terminal amino group. The loss of H_2 from a new complex formed, **9**, involves one H from the amino group of the three-membered ring and the H of the CuH group. This process implies an energy barrier (through **TS9P5**) of only 2.8 kcal/mol. The final product, **P5(H$_2$)**, corresponds to an aminoaziridine in which the Cu^+ interacts with the nitrogen of the ring.

A third mechanism involves a low-barrier internal rotation of the CuH group of complex **7b** that stabilizes the system by 10.4 kcal mol^{-1}, leading to complex **10**. The structure of complex **10** favors the interaction of the CuH group with one of the hydrogen atoms of the closest amino group, through **TS1011**. The new species **11** dissociates into **P6(H$_2$)** + H_2. The product ion so formed, **P6(H$_2$)**, isomerizes easily to a much more stable isomer, **P1(H$_2$)**.

In light of the calculated activation barriers, the first of the three mechanisms discussed above should be discarded, because it involves an activation barrier at least 10 kcal mol^{-1} higher than the other two. For **En**-d_4 this mechanism would actually correspond to a loss of D_2, which is not observed. Conversely, the other two mechanisms would lead to a loss of HD, because one of the hydrogen atoms comes from a methylene group and the second one from one of the amino groups, in agreement with the experimental evidence.[17] Attending at energy barriers involved the third mechanism described in this section, which should be dominant with respect to the second one.

(c) C−C Insertion Mechanism. Similarly to what it has been found in previous studies of reactions of bidentate bases with transition metal monocations,[10,38] Cu^+ insertion into the C−C bond is a favorable process that will lead to a bunch of reaction mechanisms. The energy profile for the corresponding reaction is presented in Figure 5.

The first step of this mechanism is the insertion of Cu^+ in the C−C bond of **En** to yield a quite stable complex, **12** (−52.7 kcal/mol), through a transition state, **TS112**, which lies 31.9 kcal/mol below the entrance channel. Once **12** is formed, Cu can serve as a carrier for the transfer of one H from one CH_2-NH_2 group to the other. A stable structure (**13**) in which Cu holds the transferred hydrogen has been located and also presents a large stability (−33.5 kcal/mol). A subsequent interaction of the hydrogen atom attached to Cu and one of the amino hydrogens would lead from **13** to **4**, through **TS134**, and subsequently to the loss of H_2. The **13** → **4** isomerization barrier lies 16.1 kcal/mol below the entrance channel. It is worth noting that **TS1213** lies 3.3 kcal/mol below the entrance channel, rendering this mechanism completely unfavorable with respect to the "carrier" mechanisms discussed above. This is consistent with the fact that this mechanism predicts, for the reactions involving **En**-d_4, the loss of H_2, which is not observed.[17]

Loss of Ammonia. To study the loss of ammonia, we have systematically considered the transfer of one H to the terminal NH_2 group from each possible CH_2 group (1,2 and 1,3 H transfer) or from the second NH_2 group (1,4-H transfer) and we have considered different starting conformations for these possible transfers. For the sake of conciseness we will discuss only those mechanisms implying lower energy barriers.

(a) 1,2-H Transfer. Let us consider the possible processes in which one of the H atoms of the methylene group is transferred to the adjacent amino group. Adduct **3c** presents the best conformation for such a transfer (see Figure 6). This 1,2-H transfer will lead directly from **3c** to **14**, through a transition state, **TS3c14**, that lies 10.6 kcal/mol below the entrance channel. Once complex **14** is formed, two alternative pathways can be envisaged depending on whether the cyclization of the $[Cu(CH)\text{-}CH_2-NH_2]^+$ moiety to yield the product ion **P1(NH$_3$)** takes place before or after the loss of ammonia. The former of these two possibilities would lead to a quite stable complex **15**, in which Cu^+ is dicoordinated to NH_3 and to a zwitterionic isomer of aziridine. Structure **15** would eventually dissociate into **P1(NH$_3$)** + NH_3, the dissociation into $CuNH_3^+$ + (cyclic)

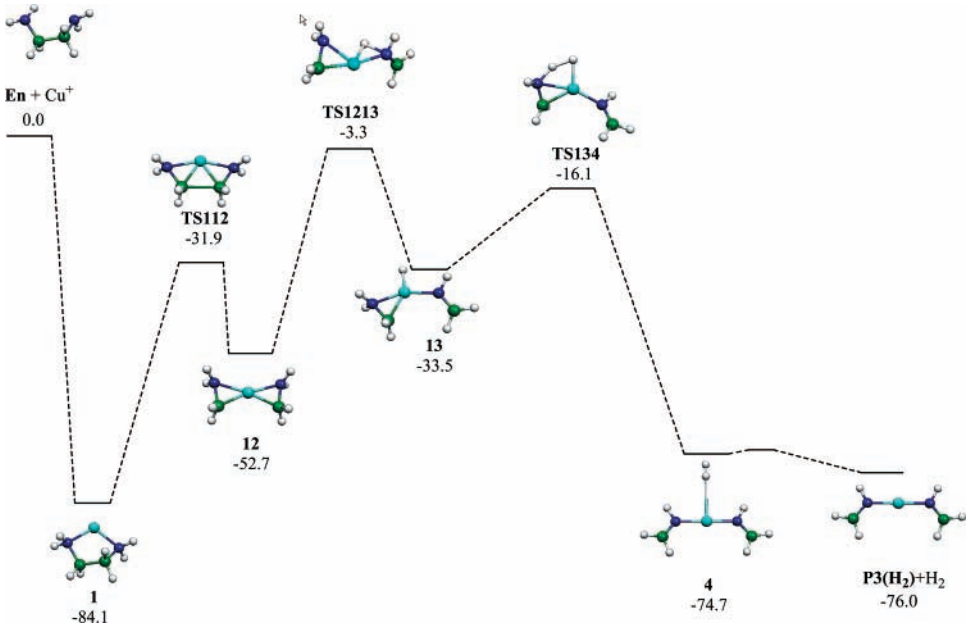

Figure 5. Energy profile for the reaction mechanism corresponding to the insertion of Cu^+ into the C−C bond of **En** leading to the loss of H_2. Energies and structures follow the same notation as in Figure 2.

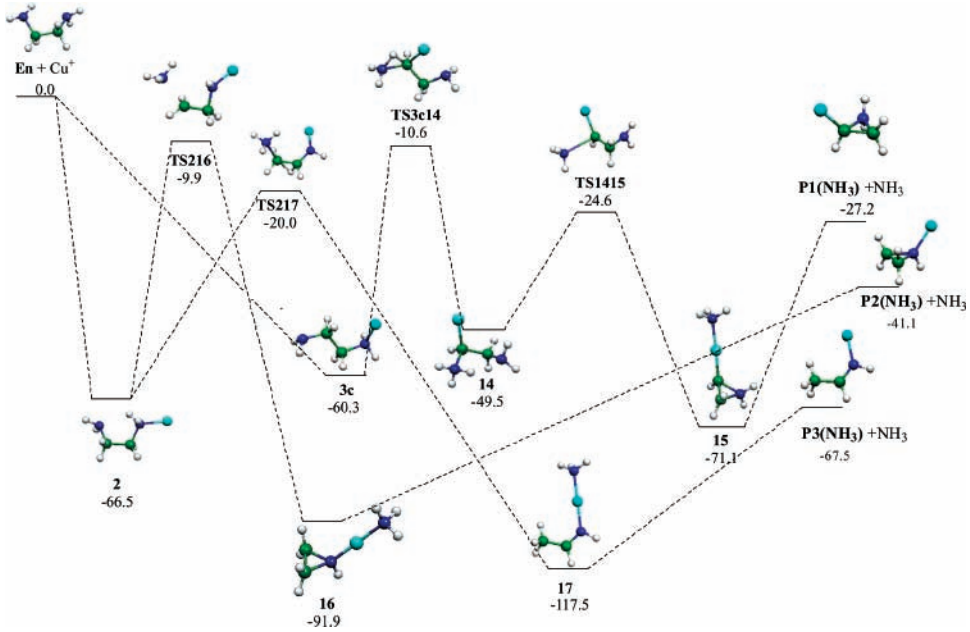

Figure 6. Energy profile of the 1,2-H transfer reaction mechanisms with origin in the **3c** adduct and the 1,4-H transfer reaction mechanisms corresponding to the with origin in the adduct **2**, leading to the loss of ammonia. Energies and structures follow the same notation as in Figure 2.

$H_2C-CH-NH_2$ being higher in energy. It should be noted that for the reactions involving the deuterated species **En**-d_4 this mechanism would yield to the loss of NH_2D, which is not observed experimentally.[17] However, the most plausible mechanisms for the loss of ammonia would be a 1,4-H transfer between the two amino groups of the **En**−Cu^+ adducts, and as we shall discuss in the next section, they are much more favorable than the 1,2-H shift presented above.

(b) 1,4-H Transfers. Two different 1,4-H shifts with the origin in **2** can be contemplated. Both are schematized in Figure 6. A direct 1,4-H transfer between the two amino groups of complex **2** produces a simultaneous cleavage of the CN bond and a concomitant cyclization of the $[H_2C-CH_2-NHCu]^+$ moiety (**TS216**), with the formation of a quite stable aziridine−Cu^+−NH_3 complex **16**, which would preferentially dissociate into **P2-(NH_3)** (aziridine−Cu^+) + NH_3 (the alternative dissociation into NH_3Cu^+ + aziridine lies 5.6 kcal/mol higher in energy). The transition state for the **2**−**16** isomerization, **TS216**, lies 9.9 kcal/mol below the entrance channel. Even though this barrier is slightly higher that the one described before for the loss of NH_3 from complexes **3c**, the process occurs in a single step; therefore it cannot be discarded as an alternative mechanism that will yield NH_3 in the case of the tetradeuterated **En**-d_4.

A more favorable mechanism is obtained if the 1,4-H transfer in complex **2** induces a simultaneous hydrogen shift between the methylene groups through the **TS217**. The structure formed is a very stable complex in which Cu^+ is bound to acetaldimine and ammonia, which would eventually dissociate into acetaldimine−Cu^+ + ammonia (the NH_3−Cu^+ + acetaldimine dissociation is less favorable by 10.0 kcal/mol). Taking into account the estimated barrier, this should be the most favorable

mechanism for the loss of ammonia, and for **En**-d_4 it would yield only NH_3, in good agreement with the experimental evidence.[17]

Loss of HCu. The loss of HCu must have its origin necessarily in species in which one of the hydrogen atoms is attached to Cu. Hence, the possible precursors would be complexes **6**, **7**, **10**, and **13** (see Figures 3−5). For reactions involving the **En**-d_4 deuterated species, the fragmentation of species **6** and **13** would yield HCu, rather than DCu, which is the loss experimentally observed. This is in agreement with the fact that the formation of both **6** and **13** involve mechanisms with activation barriers only slightly below the entrance channel. On the other hand, the loss of CuH from **6** is endothermic by 17.1 kcal/mol, with respect to the entrance channel and therefore should be discarded. The loss of HCu from complex **13** should be also a quite unfavorable process because in this case it is necessary to break two N−Cu and one C−Cu bonds.

The most favorable process, which is exothermic by 24.4 kcal mol^{-1}, would correspond to the dissociation of complex **7b** to yield $[NH_2-CH_2-NH-CH_2]^+$ as the final ion product. In the case of complex **10** the loss of CuH would yield the same ion product. However, as shown in Figure 4, this species would lose preferentially H_2. For **En**-d_4, in both cases the aforementioned fragmentations would correspond to a loss of DCu, in agreement with the experimental findings. [17]

4. Concluding Remarks

Along this paper we have presented several mechanisms for ethylenediamine + Cu^+ reactions, whose energy profiles are compatible with the observed losses of H_2, NH_3 and CuH and with the experiments involving C-tetradeuterated ethylenediamine, **En**-d_4.

The most favorable mechanism corresponds to the loss of H_2, through a mechanism in which the transition metal cation acts as a carrier. In the first steps of this mechanism a migration of a methylene group hydrogen toward the metal takes place. In subsequent steps the CuH group interacts with one of the amino hydrogens, leading finally to the loss of H_2, the product ion being a five-membered ring in which Cu^+ bridges between the N atoms of the $H_2N-CH_2-CH-NH$ moiety. This mechanism explains why for the tetradeuterated species only a loss of HD is observed.[17]

The loss of ammonia is less favorable, because all mechanisms involve higher activation barriers. The most favorable of these mechanisms implies a hydrogen shift between the two methylene groups of complex **2** that triggers a spontaneous hydrogen shift between the two amino groups, favored by the existence of a strong IHB. Accordingly, for the **En**-d_4 species only the loss of NH_3 should be observed, in agreement with the experimental evidence.[17]

The loss of HCu comes preferentially from complexes **7a**,**b**, and therefore competing with the dominant loss of H_2

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Supporting Information Available: Total energies and geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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