Unimolecular Reactivity of Strong Metal–Cation Complexes in the Gas Phase: Ethylenediamine–Cu⁺

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Abstract: The gas-phase reactions between ethylenediamine (**en**) and Cu⁺ have been investigated by means of mass spectrometry techniques. The MIKE spectrum reveals that the adduct ions $[Cu^+(H_2NCH_2CH_2NH_2)]$ spontaneously decompose by loosing H_2, NH_3 and HCu, the loss of hydrogen being clearly dominant. The spectra of the fully C-deuterated species show the loss of HD, NH_3 and CuD but no losses of H_2, D_2, NH_2D, NHD_2, ND_3 or CuH are observed. This clearly excludes hydrogen exchange between the methylene and the amino groups as possible mechanisms for the loss of ammonia. Conversely, methylene hydrogen atoms are clearly involved in the loss of molecular hydrogen. The structures and bonding characteristics of the Cu⁺(**en**) complexes as well as the different stationary points of the corresponding potential energy surface (PES) have been theoretically studied by DFT calculations carried out at B3LYP/6-311+G(2df,2p)//B3LYP/6-311G(d,p) level. Based on the topology of this PES the most plausible mechanisms for the aforementioned unimolecular fragmentations are proposed. Our theoretical estimates indicate that Cu⁺ strongly binds to **en**, by forming a chelated structure in which Cu⁺ is bridging between both amino groups. The binding energy is quite high (84 kcal mol^{-1}), but also the products of the unimolecular decomposition of Cu⁺(**en**) complexes are strongly bound Cu⁺-complexes.

Keywords: ab initio calculations · cations · copper · gas-phase reactions · mass spectrometry

Introduction

The study of metal–ion complexes is a very active area in chemistry because these complexes are of the utmost importance in biochemistry, catalysis, and molecular recognition.[1–5] An important application in this field is the design of systems able to remove heavy-metal ions from contaminated media. In this respect, bidentate or multidentate bases are suitable candidates to bind metal ions stronger than water if one plans, for example, to remove the metal from waste water streams. The ability to design a bidentate or multidentate cavity requires a good knowledge of how the metal ion interacts with the individual donor groups. In this respect, some previous studies on complexes between dimethyl ether,[6,7] Dimethoxyethane[8] polyethers,[9] glycolic acid[10] and glycerol[11] with transition-metal ions in the gas phase should be cited. However, in general, the formation of the adduct with the cation is followed by a spontaneous fragmentation of the system, so it is equally important to assure that the products of these spontaneous unimolecular processes also bind the metal cation strongly. An appropriate answer to both questions can be achieved in combined gas-phase experimental and theoretical studies. In this paper we aim at presenting such a study for a typical bidentate base such as ethylenediamine (**en**).

En is, in fact, one of the most frequently used metal ligands and its derivatives can be good precursors for the synthesis of new chelating agents.[12] Besides some of its derivatives have anti-tumor activity.[13] Many studies can be found in the literature dealing with the formation of metal complexes of **en** in solution,[14–17] but similar studies considering the structure and energy of metal complexes with **en** in the gas phase are scarce.[18] The gas-phase basicity of **en** has

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been reported in the literature, and only recently the unimolecular reactivity of the protonated form has been studied.[19] To the best of our knowledge, there are no similar studies considering the gas phase unimolecular reactivity of **en** catalyzed by transition-metal cations.

En is a paradigmatic system for conformational investigation and therefore its molecular structure has been widely studied by both experimental and theoretical methods.[20–23] The existence of intramolecular hydrogen bonds, and the possibility of intramolecular hydrogen transfer have also motivated the interest in this system.[21]

In this paper we analyze in detail the reactivity of **en** versus Cu$^+$ by means of mass spectrometry techniques and density functional theory (DFT) methods. We will focus our attention on the possible unimolecular decomposition that can occur after complex formation, because we aim at showing not only that **en** binds Cu$^+$ strongly, but also that the products of the unimolecular decomposition of Cu$^+$(**en**) complexes also bind Cu$^+$ strongly. As we will see later the most important reaction is the loss of H$_2$. Detailed ab intio studies of the mechanisms of the elimination of H$_2$ catalyzed by metals have been reported for alkanes.[1, 24–28] In this sense **en** offers an excellent benchmark system to study alternative dehydrogenation mechanisms, since the presence of two amine groups opens a large variety of possible reaction channels.

Experimental Section

All experiments were carried out using a VG analytical ZAB-HSQ hybrid mass spectrometer of BEqQ geometry, which has previously been described in detail.[29] Complexes were generated by the CI-FAB method.[30–36] The CI-FAB source was built from VG Analytical EI/CI and FAB ion source parts with the same modifications described by Freas et al.[32] A copper foil of high purity has replaced the conventional FAB probe tip. "Naked" metal ions were generated by bombardment of the target with fast xenon atoms (Xe gas 7–8 keV kinetic energy, 1–2 mA of emission current in the FAB gun). Under these experimental conditions naked metal ions, ^{63}Cu$^+$ and ^{65}Cu$^+$, were generated in a ratio close to that of their natural abundance. The organic samples were introduced via a heated probe in a non-heated closed source. In that source, we can assume that due to the relatively high pressure of the organic sample of interest (10^{-2}–10^{-3} Pa), efficient collisional cooling of the generated ions can take place. Therefore we will consider that excited states of the Cu$^+$ ions which could be formed in these experimental conditions are not likely to participate in the observed reactivity as already postulated by Hornung et al.[35] The ion beam of the Cu$^+$(**en**) adduct complexes was mass-selected (using an acceleration voltage of 8 kV) with the magnetic analyser B. The ionic products of unimolecular fragmentations, occurring in the second field-free (2nd FFR) region following the magnet, were analyzed by means of Mass-analyzed Ion Kinetic Energy (MIKE)[30, 37] by scanning the electric sector E. The CAD (Collision Activated Dissociation) experiments were carried out in the same way but introducing Ar in the cell as the collision gas. The spectra were recorded at a resolving power (R) of ~1000.

H$_2$NCH$_2$CH$_2$NH$_2$ (**en**) and H$_2$NCD$_2$CD$_2$NH$_2$ ([D$_4$]**en**) were purchased from Aldrich and were used without further purification.

Computational Details

The DFT calculations have been carried out by using the hybrid B3LYP functional. This DFT approach combines the Becke's three parameter non local hybrid exchange potential[38] with the non local correlation functional of Lee, Yang and Parr.[39] The geometries of the different species under consideration have been optimized by using the all electron (14s9p5d/9s5p3d) basis of Wachters–Hay for Cu,[40, 41] supplemented with one set of f polarization function and the 6-311G(d,p) basis set for the remaining atoms of the system. The harmonic vibrational frequencies of the different stationary points of the PES have been calculated at the same level of theory in order to classify the stationary points of the PES as local minima or transition states (TS), and to estimate the corresponding zero point energies (ZPE). In general both, geometries and vibrational frequencies obtained using the B3LYP approach are in fairly good agreement with experimental values.[42, 43]

Final energies have been obtained at B3LYP level by using an enlarged basis set, in which the standard 6-311+G(2df,2p) basis set for first row atoms is combined with a (14s9p5d/9s5p3d) Wachters-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 polarization basis for Cu. We have shown[44, 45] for some smaller Cu$^+$ complexes that the binding energies so obtained are quite reliable. Also importantly the B3LYP approach is free of the pathologies which affect the description of Cu$^+$ complexes when high level ab initio formalisms, as the G2 theory or even the CCSD(T) methods are used.[44, 46, 47]

All calculations have been done by using the Gaussian 98 program.[48]

Results and Discussion

Gas-phase reactivity: Figure 1a shows the mass spectrum, which results from the gas-phase reactions of copper ions with **en**. The existence of ^{63}Cu and ^{65}Cu isotopes leads to an easy identification of copper containing ions. In ion-molecule reaction conditions, besides production of Cu$^+$, several copper/organic product complexes were also observed. The Cu$^+$ ions react with neutral **en** to produce [Cu$^+$(**en**)] adduct ions at m/z 123, 125. The ion at m/z 121 corresponds also to an adduct ion, which involves Cu$^+$ and (**en**−H$_2$) moiety. This implies that the ion at m/z 123, as discussed latter, is a mixture of two species [^{63}Cu$^+$(**en**)] and [^{65}Cu$^+$(**en**−H$_2$)]. The observed weak ions at m/z 106, 108 (4%, with respect to the base peak) and m/z 92, 94 (4%) could correspond to [Cu$^+$,C$_2$,N,H$_5$] and to [Cu$^+$(NH=CH$_2$)] complexes, respectively. These ions could arise from the loss of NH$_3$ and CH$_3$-NH$_2$ of [Cu$^+$(**en**)] ions, respectively. The ions lower than 63 u could follow from [Cu$^+$(**en**)] which losses CuH giving rise to ion at m/z 59 ([NH$_2$-CH$_2$-CH=NH$_2$]$^+$, which turns to decompose to give ions at m/z 44, 32, 30 and 28 (C$_2$H$_6$N$^+$, CH$_3$-NH$_3^+$, CH$_2$=NH$_2^+$ and HCNH$^+$).

Unimolecular reactivity of [Cu(en)]$^+$ adduct ions: MIKES analysis (see Figure 1b and c) was performed on [Cu(**en**)]$^+$ adduct ions to obtain information related to the structure, reactivity and thermochemistry of these Cu$^+$/organic complex ions. The results presented here refer to both isotopes ^{63}Cu- and ^{65}Cu-containing species.

The MIKE spectrum of the [^{63}Cu(**en**)]$^+$ complex presented in Figure 1b shows that the m/z 123 ion gives rise to three spontaneous losses, the most important being that of H$_2$ at m/z 121 which is the base peak of the MIKE spectrum. A minor fragmentation corresponds to the loss of ammonia at m/z 106 (10%), already observed in the ion source. The MIKE spectrum presents in addition other weak peaks at m/z 92, 63 and 59 that corresponds to
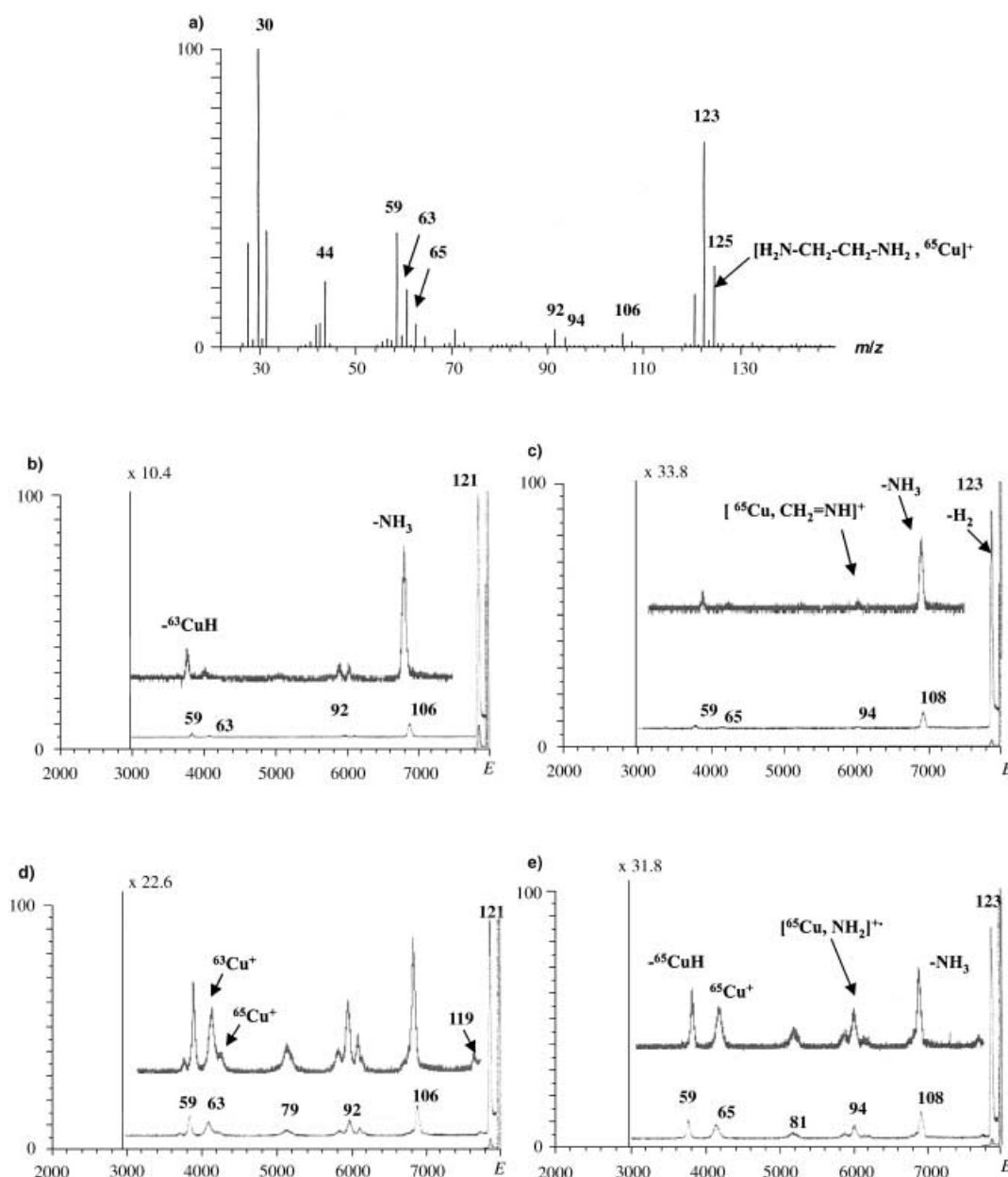
Figure 1. a) CIFAB spectrum that results from the reaction of Cu$^+$ (sputtered from a foil of copper) with neutral ethylenediamine (**en**). b) MIKE spectrum of ion at m/z 123. c) MIKE spectrum of ion at m/z 125. d) MIKE-CAD spectrum of ion at m/z 123. e) MIKE-CAD spectrum of ion at m/z 125.

[CH$_2$=NH,Cu]$^+$, Cu$^+$ and to the loss of CuH, respectively. Under collision conditions one can note, in the resulting MIKE-CAD spectrum displayed in Figure 1 d that the relative intensity of the peaks, corresponding to the loss of NH$_3$ and CuH, increases; this shows that these decomposing channels are high energy demanding processes compared with those leading to the loss of H$_2$. One can note in addition the presence of an ion at m/z 65 corresponding to ^{65}Cu$^+$ showing without ambiguity that the selected ion at m/z 123 is really a mixture of structures. MIKE and MIKE-CAD spectra (displayed in Figure 1 c and e) of [^{65}Cu(**en**)]$^+$ at m/z 125 reinforces those results.

Additional experiments have been carried out with deuterium labeled compounds in order to have additional infor-

mation on the hydrogen atoms involved in the different fragmentations (hydrogen, ammonia and copper–hydride eliminations). Figure 2a displays the isotopic mixture of different copper deuteriated [D$_4$]**en** complexes. The MIKE and MIKE–CAD spectra of ions at m/z 127 and 129 corresponding to [^{63}Cu$^+$(NH$_2$-CD$_2$-CD$_2$-NH$_2$)] and [^{65}Cu$^+$(NH$_2$-CD$_2$-CD$_2$-NH$_2$)] are presented in Figure 2b–e, respectively. We can note that the interference arising from the [Cu$^+$ (**en**−H$_2$)] ions is excluded. The loss of H$_2$ is indeed totally and specifically shifted to HD loss (with a difference of 3u). It can be observed that [^{65}Cu$^+$([D$_4$]**en**)] (m/z 129) looses HD. In the light of these results, the loss of molecular hydrogen is specific one hydrogen arises from one amino group and the other from one methylene group. Also specif-
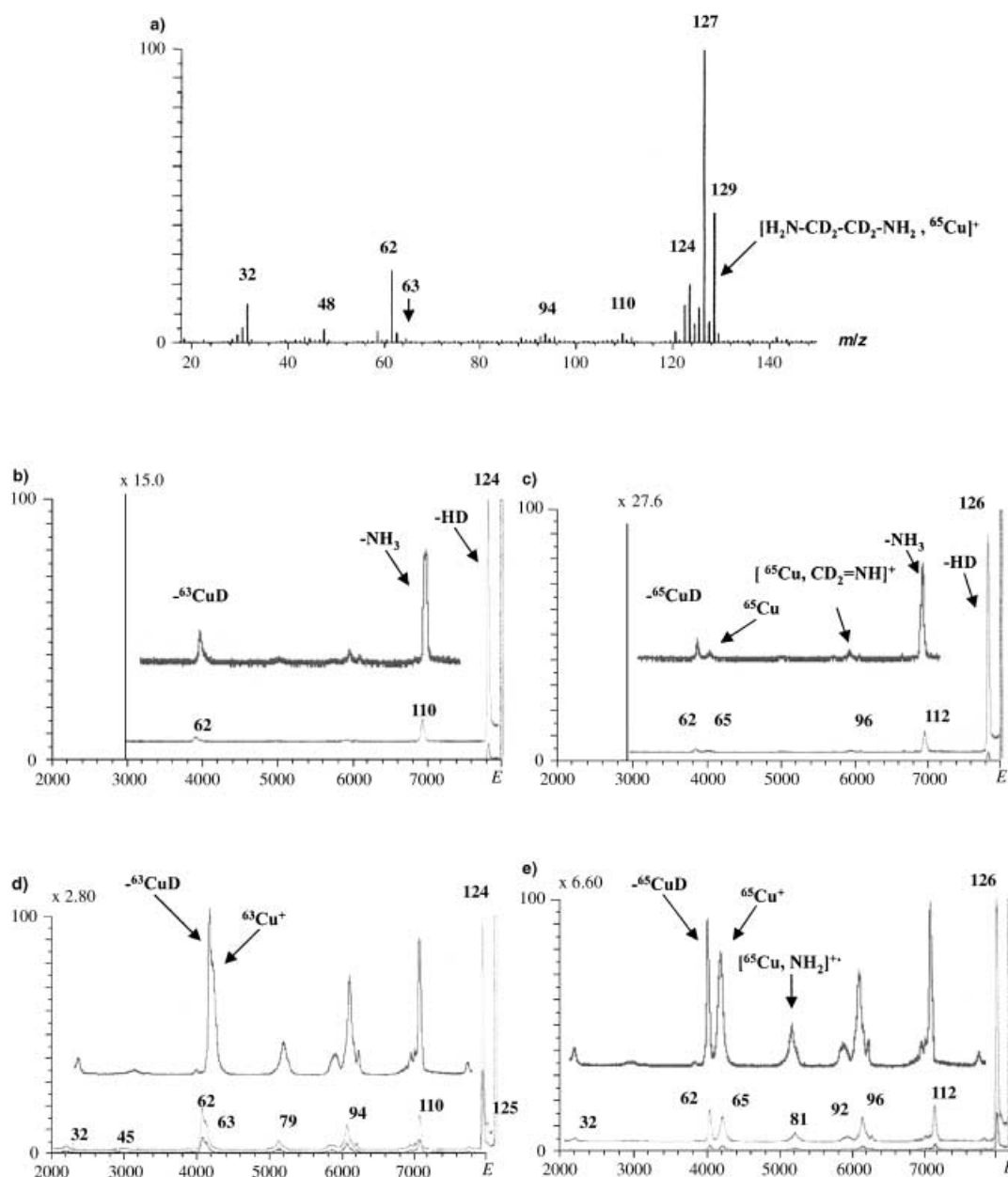
Figure 2. a) CIFAB spectrum that results from the reaction of Cu$^+$ (sputtered from a foil of copper) with neutral [D$_4$]ethylene-diaminediamine ([D$_4$]**en**). b) MIKE spectrum of ion at *m/z* 127. c) MIKE spectrum of ion at *m/z* 129. d) MIKE-CAD spectrum of ion at *m/z* 127. e) MIKE-CAD spectrum of ion at *m/z* 129.

ic are the losses of ammonia and copper−hydride. The ammonia elimination concerns exclusively the hydrogen atoms of the amino groups while the hydrogen involved in CuH elimination comes from a methylene group.

Reactions mechanisms

Cu$^+$(en) complexes: Before considering the possible mechanisms involved in the observed unimolecular reactivity of Cu$^+$(**en**) complexes, we will analyze the structure and characteristics of the possible Cu$^+$(**en**) adducts, because they are the starting point of the reaction process. As expected the most stable complex between **en** and Cu$^+$ corresponds to a

cis conformation of **en** (structure **1** in Figure 3) which permits the interaction of Cu$^+$ with both amino groups. There are, however, other conformers, namely **2** and **3**, in which the metal cation interacts only with one of the amino groups (see Figure 3). Many other species have been found as intermediates in the unimolecular decomposition of Cu$^+$(**en**) adducts and correspond to Cu$^+$ complexes involving different isomers of **en** generated by appropriate hydrogen shifts. A complete survey of the potential energy surface (PES) involves more than thirty different local minima and the corresponding transition states (TSs) connecting them. The details of the whole PES will be reported elsewhere and in the present paper, for the sake of conciseness, we will limit the
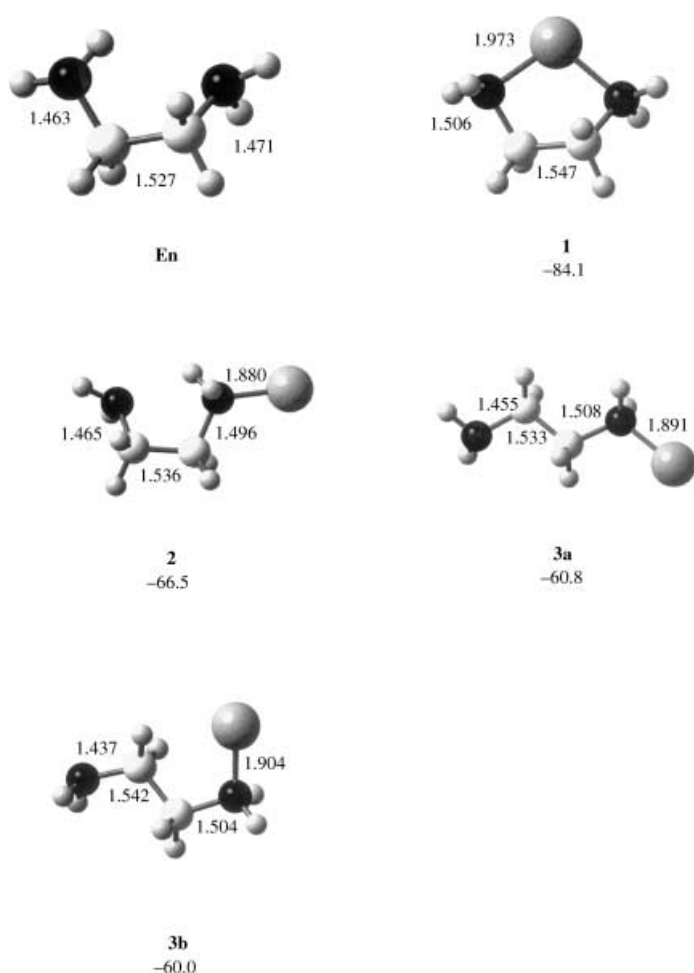
Figure 3. Structures for neutral ethylenediamine and ethylenediamine+ Cu$^+$ adducts. All distances are given in Å. Numbers refer to the relative stability (in kcal mol^{-1}) with respect the **En**+Cu$^+$ entrance channel. Black circle denotes N atoms, white circles C atoms and grey circles Cu.

discussion to the main mechanisms behind the experimental results. 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. The structures corresponding to all these species are given as Supporting Information, together with their total energies.

The binding energy, defined as the energy of the complex minus the energy of the neutral in its most stable conformation and the energy of Cu$^+$, amounts to 84.1 kcal mol^{-1} for complex **1**. This high binding energy is consistent with the experimental observation that very small loss of Cu$^+$ is obtained under MIKE conditions. The breaking of one of the N−Cu bonds of adduct **1** to give **2** implies a destabilization of the system of 17.6 kcal mol^{-1}. The *trans* form (**3a**) is further destabilized by 5.7 kcal mol^{-1} due to the concomitant breaking of the NH···N intramolecular hydrogen bond. We have also calculated the most important TS connecting the different adducts. In agreement with previous calculations on neutral **en**,[20–22] the interconversion among the different rotamers imply relatively low energy barriers. A complete survey of the interconversion mechanisms and barriers

among the different Cu$^+$(**en**) rotamers is out of the scope of our paper, but we can assume that a fast interconversion among them will take place, because the stabilization energy upon complex formation is much larger (84.1 kcal mol^{-1}) than the corresponding energy barriers (typically of the order of 20 kcal mol^{-1}).

It is worth noting that the interaction with Cu$^+$ implies a noticeable activation of the C−N bonds (see Figure 3), and in a lesser degree, of the C−C bonds. The C−N activation is larger in complex **1**, where the charge transfer to the metal is 25% greater than in the other structures.

From these structures different mechanisms can be envisaged leading to the observed experimental products: loss of H$_2$, loss of NH$_3$ and loss of CuH.

Loss of H$_2$: Among all the possible mechanisms investigated for the loss of H$_2$ the one presenting the lowest barrier involves as the key step the insertion of Cu$^+$ into one of the C−H bonds. The energy profile for such a mechanism is given in Figure 4. The suitable starting point is adduct **3a** which is connected through the transition state **TS3a4a** with complex **4a**. It can be observed that the transfer of one of the methylene hydrogens to Cu leaves a very basic CH group, so that the metal, initially attached to the amino group binds now to this CH group. From this complex an internal rotation leads to the more stable isomer **4b** (as seen in Figure 4, the internal rotation implies an almost negligible energy barrier).

An internal reorientation of the CuH group inside **4b** leads to complex **5** which is 10.4 kcal mol^{-1} more stable. From that complex Cu$^+$ acts as a carrier for a second hydrogen coming from the amino group forming the stable intermediate **6**. From this latest complex a loss of hydrogen can be produced to obtain as final product a complex between Cu$^+$ and HN-CH-CH$_2$-NH$_2$ which can exist in two different conformations, the most stable lying 65.9 kcal mol^{-1} below the initial reactants **en**+Cu$^+$.

Some other mechanisms leading to a direct loss of H$_2$ from structure **1** or mechanisms involving previous hydrogen transfer inside the **En** fragment have also been investigated and they will be reported elsewhere. However, these alternative mechanisms present energy barriers higher, involve a larger number of intermediate structures and in general leads to final structures less stable than the one reported in Figure 4. It is important to note that the fact that the loss of CuH is also observed experimentally, and that this loss corresponds systematically to CuD in the case of [D$_4$]**en** reinforces the assumption that the mechanism of Figure 4 is the most efficient one for the loss of hydrogen.

Loss of ammonia: Several mechanisms, involving H-transfers inside the **En** unit, can be envisaged leading to the loss of NH$_3$. The most efficient of these mechanisms is shown in Figure 5 and involves a transition state that is located 20 kcal mol^{-1} below the entrance channel. It corresponds to a 1,4-hydrogen transfer between the two amino groups of the Cu$^+$(**en**) adduct **2a**, which induces a simultaneous hydrogen shift between the methylene groups leading to a very stable complex **7** in which Cu$^+$ is covalently bound to
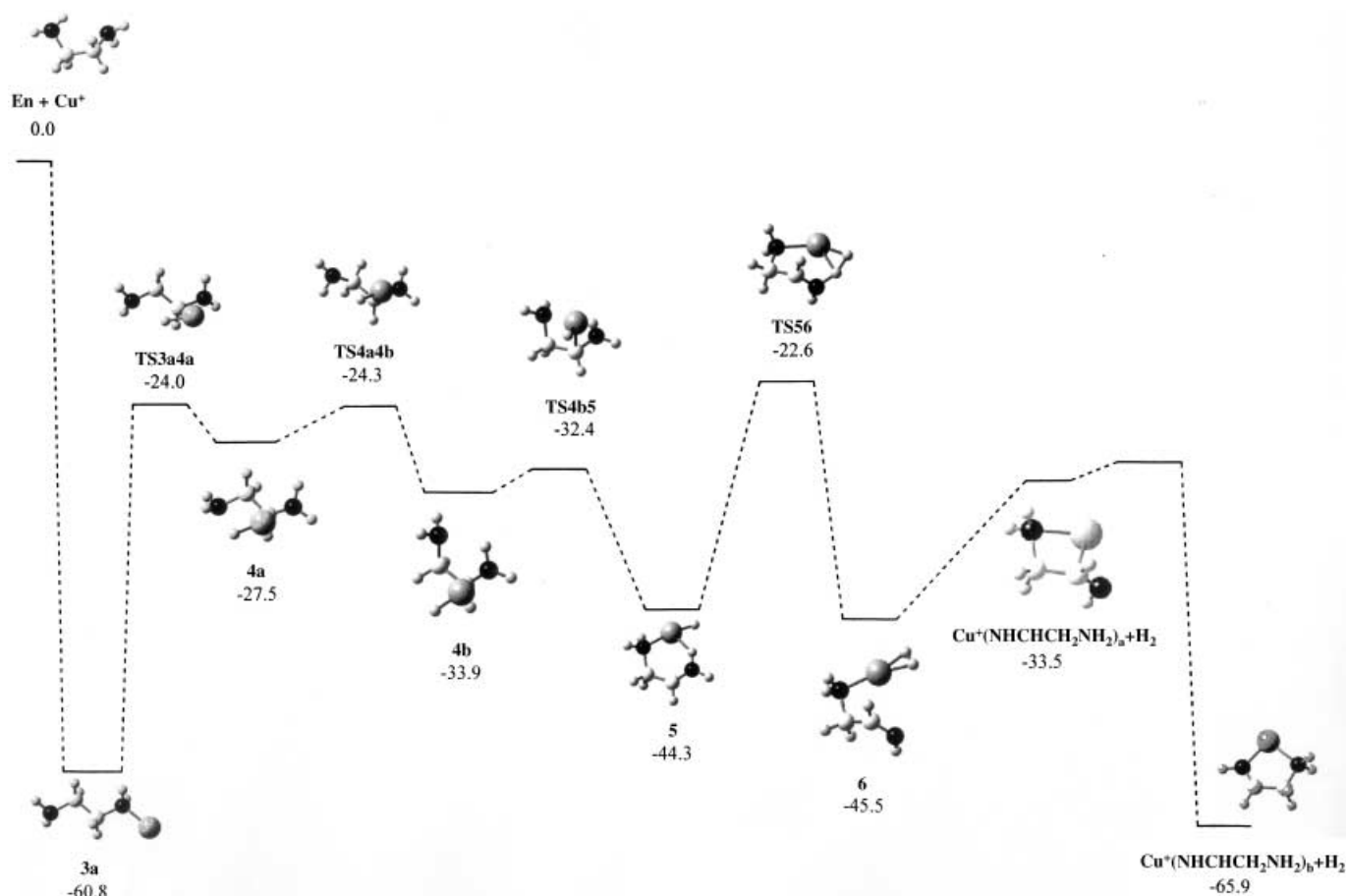
Figure 4. Energy profile for the most favorable reaction mechanisms leading to the loss of H_2. Energies and structures follow the same notation as in Figure 3.

acetaldimine and ammonia. This complex would eventually dissociate into acetaldimine−Cu^++ammonia (the dissociation into NH_3-Cu^++acetaldimine being less favorable by 10.0 kcal mol^{-1}). It is worth noting that for [D_4]**en** this mechanism would only lead to NH_3 loss in agreement with the experimental evidence. To ensure the connectivity between **2a** and **7** through the transition state **TS2a7** we have carried out ICR calculations, both forward and backward following the transition vector defining **TS2a7**. In the forward direction the 1,2-H shift between the two methylene groups leads to a breaking of the H_3C−NH_3 bond, so in the final structure the NH_3 fragment appears attached to Cu. In the backward direction, the hydrogen shift between the methylene groups disappears while a 1,4-H spontaneous transfer from the NH_3 group to the CuNH group takes place, but no local minimum corresponding to a NH_3CH_2-CH_2-$NHCu^+$ structure is found along the path. The structure shown in Figure 5 between **2a** and **TS2a7** shows the geometry of the transient species obtained in the IRC calculation, but this structure is not a minimum of the PES. In summary, on going from **2a** to **7** there is an initial barrierless hydrogen shift between the amino groups follow by a second hydrogen shift, involving an activation barrier, between the adjacent methylene groups.

It must be taken also into account that complex **2a** can be produced by a direct attachment of Cu^+ to ethylenediamine or by isomerization from the global minimum **1**.

Loss of HCu: The loss of HCu must necessarily have its origin in species in which one of the hydrogen atoms is attached to Cu. Among all the complexes studied in which a CuH subunit is present structure **4** represents the most favorable precursors. Dissociation from structure **5** is also possible and would lead to the same final product, but would imply the breaking of two bonds. The loss of CuH is exothermic, with respect to the entrance channel, by 24.4 kcal mol^{-1}, and corresponds to the dissociation of complex **4** (or **5**) to yield NH_2-CH_2-CH^+-NH_2 as ion product. In the case of [D_4]**en** the observed loss of CuD is compatible with the loss of CuH from complex **4**. It is worth noting that the loss of HCu from complexes **4** competes with the loss of H_2 discussed in previous sections. As a matter of fact, the energy required for the loss of HCu from these complexes is close to the energy barriers involved in the mechanism for H_2 loss. The alternative dissociation of these complexes into NH_2-CH_2-CH-NH_2+CuH^+ implies a much larger energy and in fact structure **4** and **5** shows that the charge in the CuH group is close to zero.

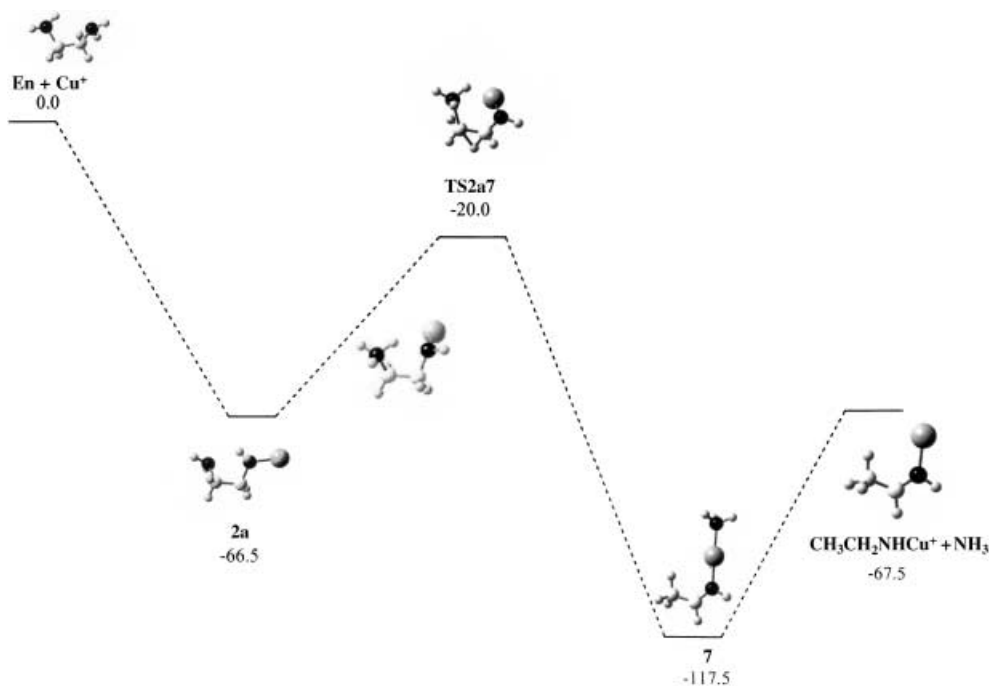 **www.chemeurj.org** *Chem. Eur. J.* **2004**, *10*, 2927–2934

Figure 5. Energy profile for the most favorable reaction mechanisms leading to the loss of NH$_3$. Energies and structures follow the same notation as in Figure 3.

Conclusions

Along this paper we have presented several mechanisms, for which the energy profiles are compatible with the observed losses of H$_2$, NH$_3$ and CuH and with the experiments involving tetra-deuterated **en**.

In the most favorable mechanism for the loss of H$_2$, Cu$^+$ plays a crucial role by acting as a "carrier" for hydrogen, connecting one of the methylene hydrogen atoms with one of the amino hydrogen atoms. Coherently, the C-tetradeuterated species only looses HD. Some of the intermediates formed in which a methylene hydrogen is attached to Cu can eventually dissociate by loosing CuH (CuD in the case of [D$_4$]**en**).

As far as the loss of NH$_3$ is concerned, the most favorable mechanism is the one with origin in adduct **2**, involving a H-transfer from one amino group to the other, which is compatible with the experimental observation that the C-tetra-deuterated species looses NH$_3$ exclusively.

The most exothermic process in Cu$^+$+ethylenediamine reactions corresponds to the loss of H$_2$ to yield Cu$^+$(NHCHCH$_2$NH$_2$) as the product ion, while the most exothermic channel for the loss of NH$_3$ to yield CH$_3$CHNHCu$^+$ lies 8.5 kcal mol^{-1} higher in energy.

Finally, it is worth mentioning that, according to our estimates, **en** binds Cu$^+$ very strongly, with a binding energy of 84.1 kcal mol^{-1}. Also importantly, all product ions of the unimolecular fragmentation of Cu$^+$(**en**) complexes also bind Cu$^+$ strongly, so Cu$^+$ is a very minority product both in MIKE and in CAD spectra.

Acknowledgement

[1] K. Eller, H. Schwarz, *Chem. Rev.* **1991**, *91*, 1121 – 1177.
[2] A. Fontijn, *Gas-Phase Metal Reactions*, North Holland, Amsterdam, **1992**.
[3] B. S. Freiser, Kluwer, Dordrecht, **1995**.
[4] A. Sigel, H. Sigel, *Metal ions in biological systems, Vol. 32, 33*, Marcel Dekker, New York, **1996**.
[5] P. B. Armentrout, *Ann. Rev. Phys. Chem.* **2001**, *52*, 423 – 461.
[6] H. Koizumi, M. Larson, F. Muntean, P. B. Armentrout, *Int. J. Mass Spectrom.* **2003**, *228*, 221 – 235.
[7] H. Koizumi, X. G. Zhang, P. B. Armentrout, *J. Phys. Chem.* **2001**, *105*, 2444 – 2452.
[8] H. Koizumi, P. B. Armentrout, *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 480 – 489.
[9] J. A. Alvarez, H.-F. Wu, C.-C. Liou, J. Brodbelt, *J. Am. Chem. Soc.* **1996**, *118*, 9131 – 9138.
[10] L. Boutreau, P. Toulhoat, J. Tortajada, A. Luna, O. Mó, M. Yáñez, *J. Phys. Chem. A* **2002**, *106*, 9359 – 9368.
[11] L. Boutreau, E. Leon, L. Rodriguez-Santiago, P. Toulhoat, O. Mó, J. Tortajada, *J. Phys. Chem. A* **2002**, *106*, 10563 – 10577.
[12] P. Hajós, *J. Chromatogr.* **2002**, *955*, 1 – 8.
[13] Y. Ogawa, M. Iwama, K. Ohgi, T. Tsuji, M. Irie, T. Itagaki, H. Kobayashi, N. Inokuchi, *Biol. Pharm. Bull.* **2002**, *25*, 722 – 727.
[14] P. Paoletti, *Pure Appl. Chem.* **1984**, *56*, 491 – 522.
[15] R. Ahlrichs, M. Ballauff, K. Eichkorn, O. Hanemann, G. Kettembach, P. Klüfers, *Chem. Eur. J.* **1998**, *4*, 835 – 844.
[16] R. J. Holmes, R. A. J. O'Hair, W. D. McFadyen, *Rapid Commun. Mass Spectrom.* **2000**, *14*, 2385 – 2392.
[17] A. Sungpet, T. Saithong, S. Kalapanulak, *J. Membr. Sci.* **2002**, *202*, 81 – 87.
[18] Y.-H. Liau, T.-M. Su, *J. Am. Chem. Soc.* **1992**, *114*, 9169 – 9177.

[19] G. Bouchoux, N. Choret, F. Berruyer-Penaud, R. Flammang, *J. Phys. Chem. A* **2001**, *105*, 9166–9177.

[20] S. J. Lee, B. J. Mhin, S. J. Cho, J. Y. Lee, K. S. Kim, *J. Phys. Chem.* **1994**, *98*, 1129–1134.

[21] M. R. Kazerouni, L. Hedberg, K. Hedberg, *J. Am. Chem. Soc.* **1994**, *116*, 5279–5284.

[22] P. Bultinck, A. Goeminne, D. Vandevondel, *J. Mol. Struct.* **1995**, *339*, 1–14.

[23] S. Kudoh, M. Takayanagi, M. Nakata, T. Ishibashi, M. Tasumi, *J. Mol. Struct.* **1999**, *479*, 41–52.

[24] K. Eller, *Coord. Chem. Rev.* **1993**, *126*, 93–147.

[25] B. S. Freiser, *Acc. Chem. Res.* **1994**, *27*, 353–360.

[26] R. Georgiadis, E. R. Fisher, P. B. Armentrout, *J. Am. Chem. Soc.* **1989**, *111*, 4251–4262.

[27] M. R. Sievers, P. B. Armentrout, *Organometallics* **2003**, *22*, 2599–2611.

[28] H. Schwarz, D. Schroeder, *Pure Appl. Chem.* **2000**, *72*, 2319–2332.

[29] A. G. Harrison, R. S. Mercer, E. J. Riener, A. B. Young, R. K. Boyd, R. E. March, C. J. Porter, *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 13–31.

[30] R. G. Cooks, *Collision Spectroscopy*, Plenum Press, New York, **1978**.

[31] J. Chamot-Rooke, J. Tortajada, J.-P. Morizur, *Eur. Mass Spectrom.* **1995**, *1*, 471–478.

[32] R. B. Freas, M. M. Ross, J. E. Campana, *J. Am. Chem. Soc.* **1985**, *107*, 6195–6201.

[33] R. B. Freas, J. E. Campana, *J. Am. Chem. Soc.* **1985**, *107*, 6202–6204.

[34] T. Drewello, K. Eckart, C. B. Lebrilla, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1987**, *76*, 13–16.

[35] G. Hornung, D. Schröder, H. Schwarz, *J. Am. Chem. Soc.* **1995**, *117*, 8192–8196.

[36] H. Mestdagh, N. Morin, C. Rolando, *Tetrahedron Lett.* **1986**, *37*, 33–36.

[37] R. G. Cooks, J. H. Beynon, R. M. Caprioli, G. R. Lester, *Metastable Ions*, Elsevier, New York, **1973**.

[38] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[39] C. Lee, W. Yang, R. G. Parr, *Phys. Rev.* **1988**, *37*, 785–789.

[40] A. J. H. Wachters, *J. Chem. Phys.* **1970**, *52*, 1033–1041.

[41] P. J. Hay, *J. Chem. Phys.* **1977**, *66*, 4377–4384.

[42] C. W. Bauschlicher, *Chem. Phys. Lett.* **1995**, *246*, 40–44.

[43] T. Ziegler, *Chem. Rev.* **1991**, *91*, 651–667.

[44] A. Luna, M. Alcami, O. Mo, M. Yanez, *Chem. Phys. Lett.* **2000**, *320*, 129–138.

[45] A. Luna, B. Amekraz, J. Tortajada, *Chem. Phys. Lett.* **1997**, *266*, 31–37.

[46] T. K. Ghanty, E. R. Davidson, *Int. J. Quantum Chem.* **2000**, *77*, 291–300.

[47] B. J. Lynch, D. G. Truhlar, *Chem. Phys. Lett.* **2002**, *361*, 251–258.

[48] *Gaussian 98*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. J. A. Montgomery, R. E. Stratmann, 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. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, revised A3 ed., Gaussian, Inc., Pittsburgh PA, **1999**.