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LETTERS

A Hydrogen-Bond Stabilized Copper Complex: Cu−Ethylenediamine

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Copper−ethylenediamine (Cu−en) is produced by the reaction of laser-vaporized Cu atoms with en vapor and studied by pulsed-field ionization zero-electron kinetic energy (PFI-ZEKE) photoelectron spectroscopy and ab initio calculations. Four possible isomers are predicted for the complex, and a monodentate structure with an internal hydrogen bond is identified. For this hydrogen-bonded structure, the adiabatic ionization potential and frequencies of the Cu−en stretch, Cu−en bend, and hydrogen-bond stretch are measured from the PFI-ZEKE spectrum, and Cu−en dissociation energies are obtained from second-order Møller−Plesset (MP2) calculations.

Ethylenediamine (en) or 1,2-diaminoethane is described as God's gift to coordination chemists and widely used as a chelating ligand in inorganic chemistry.[1,2] The ligand can adopt staggered trans and gauche conformations about the C−C bond. It is all trans in the solid state[3] and largely gauche in the liquid.[4] In the vapor phase, 10 distinct rotational isomers have been predicted,[4−7] and the most stable ones are two gauche forms, each with an intramolecular hydrogen bond H−N•••H.[6] The two gauche forms arise from different orientations of the two NH_2 groups and have a tendency of converting to the trans form with increasing temperatures[6] or IR radiation.[7] At the level of the second-order Møller−Plesset (MP2) perturbation theory, the energy difference between the two gauche forms is about 1 kJ/mol and the gauche stability relative to the trans is about 5 kJ/mol.[4] In binding with Li^+, Na^+, and K^+/K and Mg^+ metal atoms, the most stable isomer has been predicted to be a bidentate cyclic structure.[8−10] The stability of the cyclic structure is expected from the viewpoint of the chelate effect. The enthalpy of the dissociation of K^+−en has been measured through the temperature dependence of ion−molecule equilibria,[11] ionization thresholds of K−en and K_2−en have been estimated by photoionization efficiency spectroscopy,[9] and the dissociation reaction of Mg^+−en has been studied with mass-selective photodissociation spectroscopy.[10] However, there has been no experimental determination of isolated metal−en structures.

In this communication, we report the first hydrogen-bond-stabilized monodentate Cu−en complex, identified by pulsed-field ionization zero-electron kinetic energy (PFI-ZEKE) photoelectron spectroscopy and ab initio calculations. The Cu−en complex was produced by the reaction of Cu atoms and the vapor of the ligand in a supersonic molecular beam. Cu atoms were generated by laser vaporization with the second-harmonic output of a Nd:YAG laser. The molecular mass was determined by using laser photoioniztion time-of-flight mass spectrometry. The PFI-ZEKE signal was obtained by laser photoexcitation of Cu−en molecules to high-lying Rydberg states, followed by PFI of the excited molecules. A frequency-doubled dye laser, pumped by a XeCl excimer laser, was used for photoionization and photoexcitation. Details about the PFI-ZEKE experiment and apparatus were described in a previous publication.[12]

Figure 1 shows four Cu−en isomers, H-bond I, H-bond II, ring, and trans, obtained from MP2/6-311+G(d,p) calculations.[13] The two H-bonded structures are formed by Cu binding with a single nitrogen of either of the two en gauche forms. They have nearly an identical Cu−N distance but a slightly different N•••H bond length and electronic energy. The major difference between these two monodentate structures is the dihedral angle ∠Cu−N−C−C, which is 72.0° in H-bond I and −169.5° in

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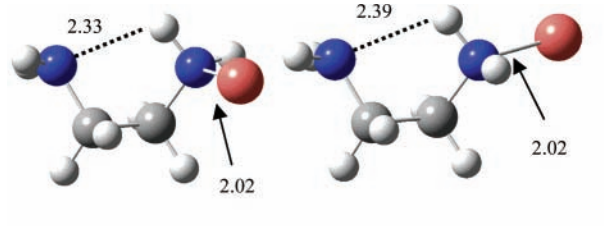
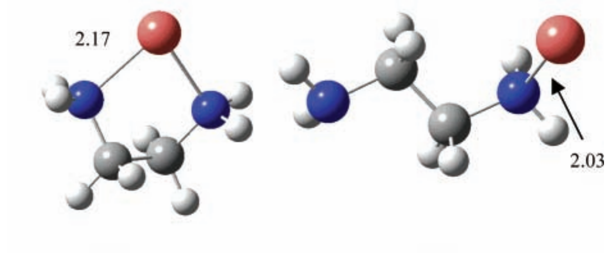


(a) H-bond I, 0 kJ/mol **(b) H-bond II, 2 kJ/mol**



(c) ring, 4 kJ/mol **(d) trans, 14kJ/mol**

Figure 1. Four isomeric structures of Cu−en along with the relative equilibrium energies from the MP2/6-311+G(d,p) calculations: Cu (orange), N (blue), C (gray), and H (white).

H-bond II. The ring structure is formed by Cu bound with two nitrogens of a gauche en and has a 2-fold axis passing through the Cu atom and the middle point of the C−C bond. This bidentate isomer has a longer Cu−N distance and is located a few kJ mol^{-1} above the H-bonded structures. The trans conformer is formed by Cu binding to a single nitrogen of a trans en of C_i symmetry and has the highest energy among the four isomers. We also calculated a structure formed by Cu binding with a trans en in C_{2h} symmetry, but it had an imaginary frequency.

The theoretical adiabatic ionization potentials (AIPs) and metal−ligand bond dissociation energies (D_0 and D_0^+) of these isomers are listed in Table 1. These energies include vibrational zero-point corrections. Although the most stable isomer of the neutral complex is in the H-bond I conformation, the bidentate structure has the highest stability in the ionized form. For all isomers, the binding is dramatically enhanced due to the additional charge-dipole interaction in the ion. The binding difference between the neutral and ionized species is about five times in the monodentate isomers, whereas the difference is seven times in the bidentate isomer. The largest binding difference leads to the lowest ionization energy of the ring structure.

Figure 2 presents the measured PFI-ZEKE spectrum and spectral simulations from the four isomeric structures of the Cu−en complex. The experimental spectrum has a spectral resolution (full width at the half-maximum height) of ∼5 cm^{-1}. The first strong photoelectron band appears at 43491(5) cm^{-1} or 5.3922(6) eV, which corresponds to the AIP of the complex. Above the AIP, the photoelectron bands largely arise from the transitions of the electronic and vibrational ground levels of the neutral complex to various vibrationally excited levels of the electronic ground state of the ion. Below the AIP, the spectrum shows a number of weak bands originating from the excited vibrational levels of the neutral electronic ground state. The simulations are calculated within the harmonic oscillator and Franck−Condon approximations, using the equilibrium geometries, vibrational frequencies, and normal coordinates of the neutral and ion complexes.[14] Spectral broadening is simulated by giving each line a Lorenztian line shape with the line width of the experimental spectrum. The calculated AIP of each isomer is referenced to the experimental value, but the vibrational frequencies are not scaled in these simulations. It is evident from the figure that the simulation from the H-bond I isomer is in nice agreement with the experiment, while others are not. This comparison shows that the Cu−en complex probed by PFI-ZEKE spectroscopy is in the H-bond I structure and that there is no clear evidence of significant spectral contributions from the H-bond II, ring, or trans isomers. Searches of PFI-ZEKE signals around predicted ionization potentials of these isomers were not successful. These higher-energy isomers may initially be formed but quickly relaxed to the lowest-energy structure in supersonic expansions.

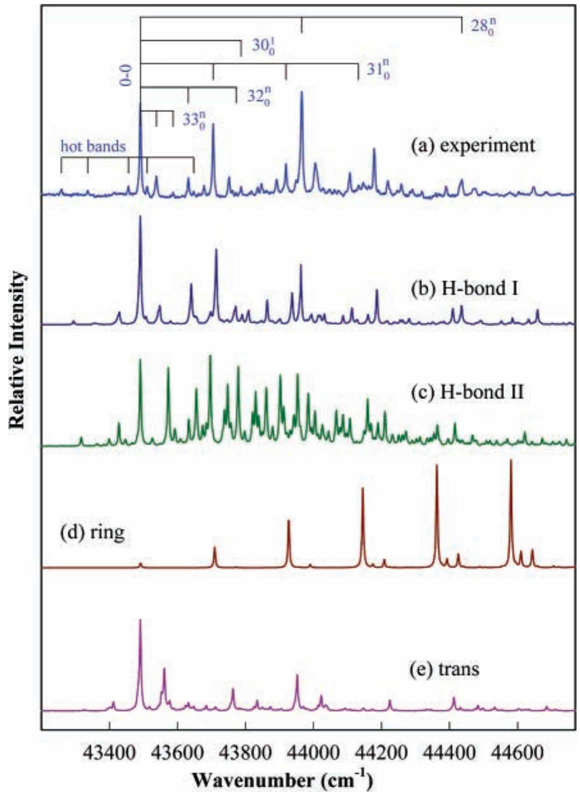


Figure 2. The PFI-ZEKE spectrum of Cu−en seeded in Ar (a) and simulations (80 K) of Cu−en four isomers (b−e).

TABLE 1: AIPs and Metal−Ligand Bond Dissociation Energies (D_0 for the Neutral Species and D_0^+ for the Ion) of Four Isomers from the MP2/6-311+G(d,p) Calculations

	AIP/eV	D_0/kJ mol^{-1}	D_0^+/kJ mol^{-1}
H-bond I	5.03	53.6	268.0
H-bond II	4.99	52.8	270.9
ring	4.08	50.1	355.7
trans	5.18	47.4	247.0

The spectral assignment is trivial with the excellent agreement between the measured and calculated spectra in parts a and b of Figure 2. In Figure 2a, we only label the PFI-ZEKE bands from transitions involving single ion vibrational mode (e.g., 28_0^n, 30_0^1, 31_0^n, 32_0^n, 33_0^n) and those from hot transitions. Other bands arise from combinational transitions with two or more of these ion modes. Fundamental frequencies obtained from the spectral assignment are summarized in Table 2, along with MP2 values of the H-bond I structure. The vibrational assignment indicates the major vibration associating with each frequency. The spectrum probes the Cu−N stretch, Cu−N−C bend, Cu−N−C−C torsion, H-bond stretch, and NH_2 rock motions. The Cu−en and H-bond vibrations are the most important normal modes in defining the metal−ligand binding and molecular structure. The Cu−N stretch frequency increases from the

TABLE 2: AIP (cm^{-1}) and Vibrational Frequencies (cm^{-1}) of the H-bond I Cu−en Complex

	ZEKE	MP2	
AIP	43491	40600	
ν_{28}^{+}	474/	473/353	Cu−N stretch
ν_{30}^{+}	296/	318/250	NH_2 rock
ν_{31}^{+}/ν_{31}	214/197	223/197	H-bond stretch
ν_{32}^{+}/ν_{32}	141/121	150/133	Cu−N−C bend
ν_{33}^{+}/ν_{33}	47/35	57/62	Cu−N−C−C torsion

neutral complex to the ion as ionization enhances the metal−ligand binding. The H-bond stretch frequency increases from the free ligand to the neutral and to the ion, as the partial charges become more negative on the H-bonded nitrogen and more positive on the H-bonded hydrogen. The Mulliken charges on nitrogen are calculated to be −0.430, −0.529, and −0.573 in the free ligand, the neutral, and ionic complexes, respectively; whereas the corresponding charges on hydrogen are 0.265, 0.295, and 0.325.

The Cu−en complex may be compared with the previously studied K−en complex. In the potassium case, the most stable neutral structure is a five-membered ring with the metal atom bound to two nitrogens.[9] The dissociation energy of the ring structure is about twice that of the monodentate isomers. In the copper case, the H-bonded isomer is slightly more stable, an indication that the overall stabilization of the N···H and Cu−N bonds is larger than the two Cu−N bonds of the bidentate structure. This binding difference likely arises from the differential electron repulsion between the metal 4s electron and the nitrogen electron lone pair. The electron repulsion is larger for Cu than K, since the metal 4s orbitals and the metal−nitrogen distances are smaller for the heavier atom.

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