Comparative Density Functional Theory Study of the Binding of Ligands to Cu^+ and Cu^{2+}: Influence of the Coordination and Oxidation State

Jean-Marie Ducéré, Annick Goursot, and Dorothée Berthomieu*,†

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 CNRS-ENSCM-UM1, Institut Gerhardt FR 1878, ENSCM, 8, rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

Received: May 12, 2004; In Final Form: October 23, 2004

BP86, B3LYP and MP2 methods, generally used to study large systems containing transition metals, were compared for their ability to accuratly evaluate bond dissociation energies of copper complexes. Various $[Cu-L]^+$ and $[Cu-L]^{2+}$ complexes in which L are small ligands and the higher coordinated complexes, $[Cu(NH_3)_4]^+$ and $[Cu(NH_3)_4]^{2+}$ were studied. For monoligated complexes, the BDEs calculated by the three methods differed by 2 to 60 kcal/mol, the larger differences being obtained for $[Cu-L]^{2+}$ complexes. The BDEs calculated using the B3LYP functional were in general close to the experimental values whereas the BDEs calculated using the BP86 functional were too high and the BDEs calculated using the MP2 were too low. If we rank the whole ligands according to their increased bond strength, the resulting orders obtained with the three methods are different for the $[Cu-L]^+$ complexes, the B3LYP giving the same order as the experimental one. This result indicates that the BDEs of $[Cu-L]^+$ complexes are better modeled using the B3LYP than using the BP86 and MP2 methods. For $[Cu-L]^{2+}$, B3LYP also gave the most reliable results whereas BP86 gave too large BDEs and MP2 gave too small BDEs. However, symmetries of ground states can be different using DFT and post-Hartree−Fock methods. For $[Cu-N_2O]^{2+}$ the use of the B1LYP provides a better symmetry of the complex than the B3LYP, as has been recently shown in the literature for $[Cu-H_2O]^{2+}$. MP2 led to an incorrect bent structure for $[Cu-N_2]^{2+}$ in contrast to a linear structure obtained with the other methods, including CCSD(T). However, due to the lack of experimental data for $[Cu-L]^{2+}$ complexes and to contrasted results for the methods, it is not possible to conclude definitely. For the high coordinated complexes $[Cu(NH_3)_4]^+$ and $[Cu(NH_3)_4]^{2+}$, the PBE calculation method was used in addition to the BP86, B3LYP and MP2. The BDE values were very close to each other when there is no change of the oxidation state during the reaction. On the basis of these calculations, the choice of the method was less crucial for high coordinated complexes $[Cu(NH_3)_4]^+$ and $[Cu(NH_3)_4]^{2+}$ so long as the oxidation state remained the same during the reaction. In contrast, when $[Cu(NH_3)_4]^{2+}$ is reduced in $[Cu(NH_3)_3]^+$ and NH_3, the BDE calculated using the four methods were markedly different.

Introduction

The complexes resulting from the interaction between transition metal ions and organic molecules or biomolecules constitute an important class of organometallic compounds, which can be found in catalytic materials and proteins. Their study can bring useful information on the role of the metal in the catalytic activity of these compounds. The fundamentals of the metal−ligand interactions and of the electronic structures of the complexes have been defined—even if not completely achieved—from experiments and quantum chemical calculations, performed on complexes containing small ligands.[1,2] Copper ions play a crucial role in many catalytic and oxido-reduction reactions.[3] For instance, in environmental chemistry, copper-exchanged zeolites are efficient catalysts to remove NO_x from gaseous effluents.[4] Only a few experimental data relate to the thermochemistry of Cu^+ cations coordinated with small ligands. The situation is even worse as far as Cu^{2+} is concerned. This is due to the difficulty to generate and isolate Cu^+ and Cu^{2+} complexes. However, recent experimental studies provided the first thermodynamic data characterizing $[Cu-NH_3]^{2+}$ and $[Cu-H_2O]^{2+}$, thus demonstrating that these unsaturated adducts are long-lived species.[5] The computed thermodynamic properties of Cu complexes reported in the literature were obtained using quantum calculations with either post-Hartree−Fock or high-correlated methods. The theoretical modeling of copper complexes is, however, very complex and these methods were shown to be unreliable in some situations.[6−8] Furthermore, these methods cannot be used for large systems, such as materials or biological systems, for which only DFT-based methods are able to handle d-electron correlation. To apply DFT to large organometallic compounds containing copper, it is prerequisite to test how accurately this method models chemical properties. Because biological and chemical processes most frequently involve oxido-reduction reactions and high-coordinated transition metals, it is important to test how accurately changes of oxidation state and coordination can be handled theoretically. Previous studies led to the conclusion that the DFT based on hybrid functionals gave binding energies in good agreement with the experimental values for Cu^+.[6]

In this work, we studied a series of small complexes involving both Cu^+ and Cu^{2+} to evaluate the accuracy with which binding energies can be determined by using DFT methods, in comparison with experimental values. We have also compared DFT

* Corresponding author. E-mail: bertho@univ-montp2.fr.
† Laboratoire de Matériaux Catalytiques et Catalyze en Chimie Organique.

10.1021/jp047971b CCC: $30.25
Published on Web 12/24/2004

TABLE 1: BDEs of $[Cu-L]^+$ Complexes

		BDE (kcal/mol)				
$[Cu-L]^+$	symmetry	BP86/BI	B3LYP/BI	MP2/BI (ROMP2/BI)	exp	theo
						54.7−56.1 MCPF[29,32,a]
						55.0 MP2[33,a]
					60 GIBMS[31]	56.2 B3LYP[34,a]
$[Cu-NH_3]^+$	$\sim C_{3v}$	58.7	53.5	43.0	56.7 GIBMS[12]	52.3 G2[34,a]
$[Cu-CO]^+$	$C_{\infty v}$	44.1	34.9	26.1	35.4 ± 1.6 GIBMS[35]	33.4 MCPF[36,c]
						39 MCPF[38,a]
$[Cu-H_2O]^+$	C_1	38.0	36.0	28.7	38.4 ± 1.8[37]	37.7 MP2[33,b]
$[Cu-H_2O]^+$	C_s			28.7		
$[Cu-H_2O]^+$	C_{2v}			28.7		
						26.9−28.3 B3LYP[14,a]
						CCSD(T) 28 ± 8;[13] 23.4;[14,a] 19.8−21.7[39,a]
$[Cu-NO]^+$	C_s	37.0	25.8	12.5 (16.0)	26 ± 1.15 GIBMS[14]	30.0 B3LYP[39,b]
						31.7 B3LYP[40,a]
$[Cu-N_2O]^+$	$C_{\infty v}$	33.0	26.9	20.3		29.7 CCSD(T)[40,a]
						24.5 B3LYP[40,a]
$[Cu-N_2]^+$	$C_{\infty v}$	26.5	20.8	13.2	21.2 ± 7[41]	22.2 CCSD(T)[40,a]
$[Cu-ONO]^+$	C_s	25.3	20.1	10.6		
$[Cu-NO_2]^+$	C_{2v}	21.6	11.7	0.6(6.8)		
						23.5 B3LYP[40]
$[Cu-ON_2]^+$	C_s	20.3	19.5	12.4		24.5 CCSD(T)[40,a]
$[Cu-O_2]^+$	triplet, C_s	17.1	11.4	<0		9.7 CCSD(T)[13]
$[Cu-O_2]^+$	C_{2v}			<0(1.8)		

[a] ZPE correction and no BSSE correction. [b] No ZPE and no BSSE corrections. [c] $T = 298$ K.

results with those provided by the post-Hartree−Fock MP2 method and the high-correlated CCSD(T) method. We have focused our interest on $[Cu-L]^+$ and $[Cu-L]^{2+}$ complexes containing NH_3, H_2O, CO, NO, N_2O, NO_2, N_2, and O_2 ligands, which are involved in many reactions. Two model Cu complexes, $[Cu(NH_3)_{x=1,4}]^+$ and $[Cu(NH_3)_{x=1,4}]^{2+}$, were chosen to study the changes in the properties with increasing the metal coordination, higher coordination being the most frequent in chemical and biological processes, as well as the change of copper oxidation state.

Methodology

The methods considered include DFT with the BP86, PBE, and B3LYP functionals and also the MP2 and CCSD(T) methods. Energy and frequency calculations were performed on fully optimized geometries, without applying symmetry constraints. The basis set superposition error corrections were evaluated using the counterpoise correction.[9] Unscaled values were used for zero-point vibrational energy corrections for energy values. Conversions from ΔU to $\Delta H = \Delta U + \Delta(pV)$ use the ideal gas law to calculate $\Delta(pV) = RT\Delta n$, where Δn is the change in the number of gas-phase molecules in the reaction. Thermal corrections were calculated for the evaluation of reaction enthalpies ΔH and Gibbs energies ΔG at 298 K, using standard statistical mechanic formulas in the independent mode, harmonic oscillator, and rigid rotor approximations, using our ab initio results. The enthalpy and entropy have been evaluated according to the development given in McQuarrie.[10]

Ionization energies of Cu^+ (IE) were calculated as the difference between the internal energies of Cu^{2+} and Cu^+.

The extended Wachters basis set (8s6p3d) contracted according to (62111111/511112/311) was used for copper and a standard 6-311+G(2d,2p) basis for H, C, O, N, with the label BI. Standard 6-31G(d) for copper and standard 6-311+G(2d, 2p) for N and O are labeled BII. The extended Wachters basis set (8s6p3d) was used for copper and a standard 6-31G(d) basis for H, C, O, N, with the label BIII. Transition states were calculated using the Synchronous Transit-Guided Quasi-Newton method and characterized as saddle points containing one imaginary frequency. These calculations were carried out with the Gaussian 98/DFT quantum chemical package, version A11 and Gaussian03, version B5.[11]

Results and Discussion

Most of the experimental data on $[Cu-L]^+$ and $[Cu-L]^{2+}$ were obtained by guided ion beam mass spectrometry (GIBMS) in which the derived thresholds and bond energies correspond to 0 K thermochemistry. The bond dissociation energies, BDEs, are defined as the difference of molar enthalpies between products and reactants at 0 K $[H(Cu^{+/2+}) + H(L) - H(Cu^{+/2+}-L)]$. The analysis of the trends in metal−ligand binding energies was based on the $[Cu-L]^+$ and $[Cu-L]^{2+}$ complexes, in which the ligands can bind to the metal through various modes (σ- and π-donation). We have also investigated sequential copper-ammonia binding energies of $[Cu-L_{x=1-4}]^+$ and $[Cu-L_{x=1-4}]^{2+}$ to know how they are modified upon increased Cu^+ and Cu^{2+} coordination. Because, in the related experimental results, the BDEs were corrected and given at 298 K instead of 0 K by the authors,[12] for consistency, our calculated BDEs were given at 298 K for these complexes. Comparative calculations using the most frequently used functionals, BP86 and B3LYP, and post-Hartree−Fock were performed. The PBE functional was also used for the sequential copper−ammonia binding energies.

$[Cu-L]^+$. The three methods, BP86, B3LYP, and MP2 were first used to calculate the BDE of Cu^+ complexes containing NH_3, H_2O, CO, N_2O, NO_2, O_2, and N_2 (Table 1). For several complexes, various conformers and isomers were also identified (Figure 1). The isomers and conformers that were either already studied or known to be less stable were not studied. For instance, because O-end coordination for NO and CO to Cu^+ is known to lead to less stable structures,[13−15] the N-end and C-end addition to Cu^+ were studied. In the case of N_2O and NO_2, various structures coming from addition with N or O to Cu^+ were calculated. Figure 1 shows that, whatever are the methods, the symmetries are comparable, but not the bond lengths and angle values.

We have focused our interest on metal−ligand bonding energies to test how accurately these thermochemical parameters can be reproduced. The BDEs obtained from BP86, B3LYP, and MP2 methods are compared in Table 1. Whatever is the

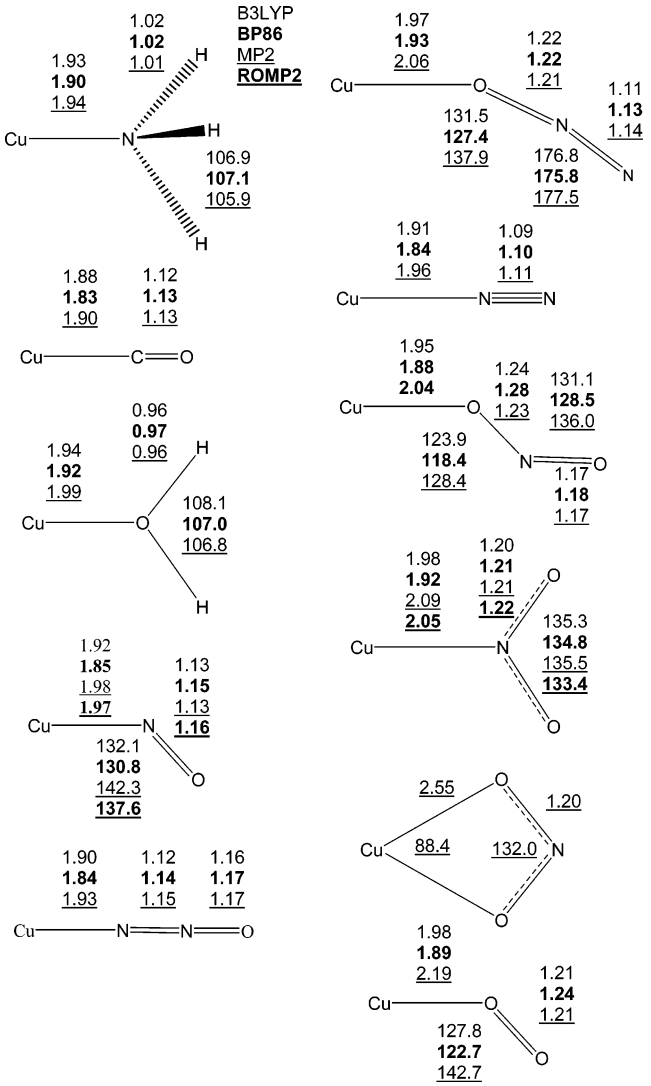

Figure 1. Structure parameters of calculated $[Cu-L]^+$ using B3LYP, BP86, MP2, and ROMP2 and the BI basis set. Bond distances are given in Å and angles, in deg.

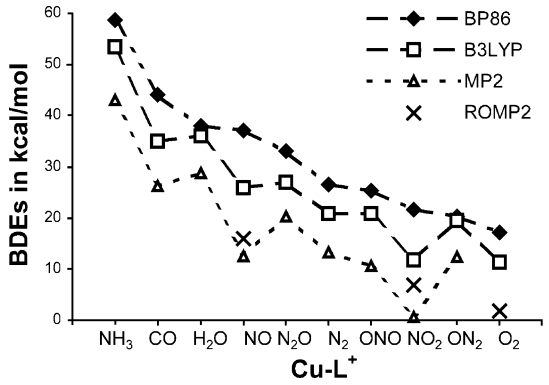

Figure 2. Calculated bond dissociation energies of $[Cu-L]^+$ using BP86, B3LYP, MP2, and ROMP2 and the BI basis set in kcal/mol.

ligand, the bond energy is always higher with DFT than with MP2. As reported in Figure 2, the BDE values are ranked as follows: BP86 > B3LYP > MP2. According to an order of increasing bond strength for each ligand, the resulting BDE order depends on the method. For instance, using BP86, the BDE of $[Cu-NO]^+$ is higher than the BDE of $[Cu-N_2O]^+$, whereas it is the opposite in the B3LYP and MP2 calculation. The BDE order is $[Cu-NH_3]^+$ > $[Cu-CO]^+$ > $[Cu-H_2O]^+$ > $[Cu-NO]^+$ > $[Cu-N_2O]^+$ > $[Cu-N_2]^+$> $[Cu-ONO]^+$ > $[Cu-NO_2]^+$ > $[Cu-ON_2]^+$ > $[Cu-O_2]^+$ with BP86 whereas the B3LYP gives a different order for many complexes such as $[Cu-CO]^+$ and $[Cu-H_2O]^+$, or $[Cu-NO]^+$ and $[Cu-N_2O]^+$. Different BDE orders are also obtained using MP2, in particular no stable $[Cu-O_2]^+$ complex, in contrast with our DFT results and previous CCSD(T) work.[13] Our calculations showed that MP2 does not perform well also for the two other ligands NO and NO_2. The erroneous BDE values calculated using MP2 originate from difficulties in obtaining the right orbitals,[6,8] but also from spin contamination and BSSE corrections. Indeed, as reported in Table 1 and in Figure 2, spin contamination contributes to lower the metal−ligand bond interaction, because restricted open-shell MP2 calculations (ROMP2) lead to larger bond energies, in better agreement with the other methods and with experiment. ROMP2 is also providing more accurate IR normal modes for $[Cu-NO]^+$. In fact, the ν_{NO} vibration (1876 cm^{-1}) calculated with ROMP2 is close to the experimental value (1904 cm^{-1}) whereas it is abnormally high (3410 cm^{-1}) without the constraint on the α and β manifolds. BSSE correction may also be overestimated (5.2 kcal/mol), contributing to the underestimation of the BDE. In the case of $[Cu-O_2]^+$ complex, the addition of the BSSE correction led to a negative BDE: the calculated BDE was 2.9 kcal/mol without the BSSE correction of 4.5 kcal/mol.

To our knowledge, there are only few experimental data for the BDEs of Cu^+ with small molecules (Table 1). Considering that the most reliable calculated values are those that match experimental values, B3LYP appears as the most reliable method, as has already been proposed.[6,8] If the largest error of the HF approach (MP2 or ROMP2) is the underestimation of the metal−ligand interaction,[16] in contrast, BP86 overestimates generally the metal−ligand bonding. Using these exchange and correlation functionals, Cu binds more strongly CO than H_2O. This wrong BDE order would originate from the self-interaction problem related to the DFT method. Due to the admixture of HF exchange, the relative stabilities are better reproduced, the B3LYP order being the same as the experimental one, i.e., $[Cu-NH_3]^+$ > $[Cu-H_2O]^+$ > $[Cu-CO]^+$ > $[Cu-NO]^+$. To enlarge the data used for our analysis, theoretical BDE values from the literature are also presented in Table 1. Differences between some of the values originate from differences in basis sets used for the same level of calculation and also from the fact that BSSE or ZPE corrections (which can be scaled or not by empirical factor) were not added in some calculations. Therefore, BDEs from referred results can be in better agreement with experiment than the values in this work and vice versa. For instance (Table 1), the 56.2 kcal/mol B3LYP value for $[Cu-NH_3]^+$ calculated with a B3LYP/6-311+G(2df,2p)//B3LYP/6-311G(d,p) without BSSE correction and with scaled ZPE is higher than the 53.5 kcal/mol B3LYP/BI value and closer to the experimental values (60 and 56.7 kcal/mol). In contrast, the 26.9 and 28.3 kcal/mol B3LYP values for $[Cu-NO]^+$ calculated with a Wachters supplemented and Stuttgart/Dresden basis set, respectively, and without BSSE correction are higher but not as close to the experimental value as the 25.8 kcal/mol B3LYP value of the present work. Published results from other methodologies, CCSD(T) and MCPF, are not as close to the experimental values as B3LYP calculations. The best ability of B3LYP to reproduce experimental BDEs is also illustrated in Figure 3. A correlation has been proposed between neutral ligand proton affinities and $[Cu-ligand]^+$ BDEs yielding a useful ladder of values for metal ion affinity of neutral compounds.[14,17,18] In Figure 3, ligand experimental proton affinities[19]

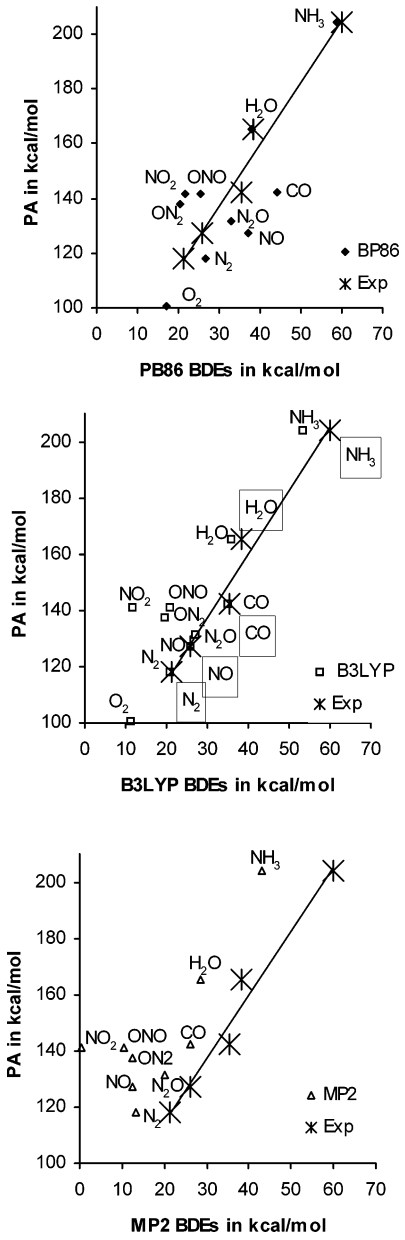

Figure 3. Comparison of calculated and experimental BDEs of $[Cu-L]^+$ with L proton affinities, PA, in kcal/mol. The straight line corresponds to the correlation of experimental BDEs of $[Cu-L]^+$ with PA of L, in kcal/mol. The experimental values are labeled with a square, only on the BL3YP graph.

are expressed as a function of both calculated and available experimental BDE values. The best linear correlation between experimental proton affinities and calculated BDE values occurs for the B3LYP set. Our calculated N_2O, NO_2, and O_2 BDE values are also reported on the graph although no experimental values are available: we can see that the values corresponding to NO_2 and ON_2 ligands deviate from the linear fit, the deviations being large whatever are the methods. These deviations originate from two different reasons. For NO_2, O- and N-ends can bind to copper, whereas the same proton affinity has been assigned to the isomers HNO_2^+ and $HONO^+$, only one experimental value being available for NO_2. This approximation introduces an error contributing to the deviation from linear correlation. For N_2O, the O proton affinity (137.6 kcal/mol) is higher than the N proton affinity (131.5 kcal/mol) whereas the calculated BDE value for $[Cu-ON_2]^+$ is lower than for $[Cu-N_2O]^+$. For this ligand, the increase of the proton

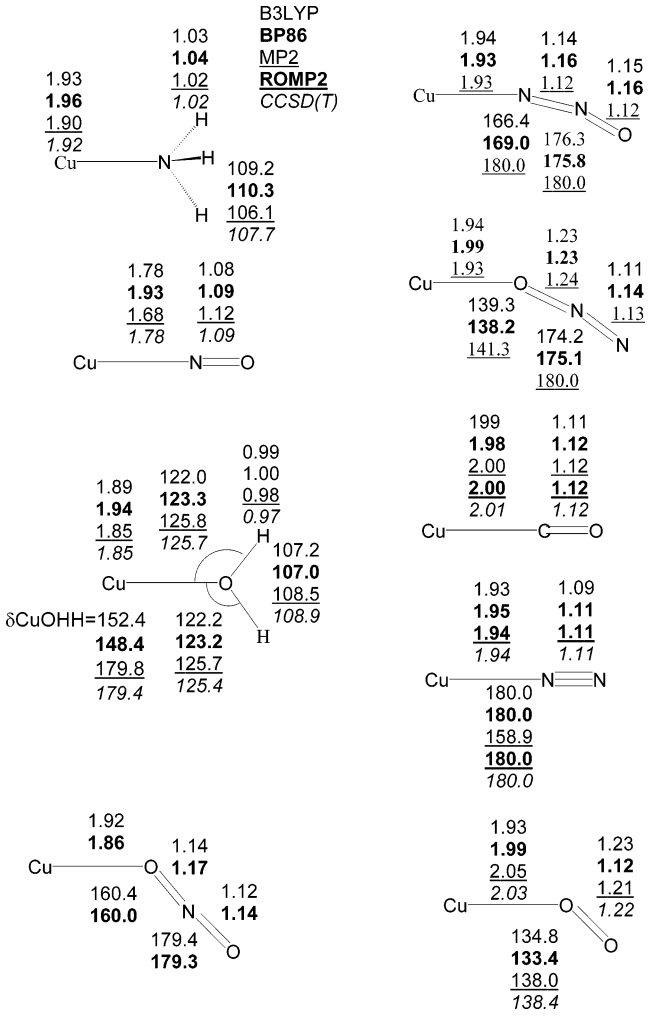

Figure 4. Structures parameters of calculated $[Cu-L]^{2+}$ using B3LYP, BP86, MP2, and ROMP2 and the BI basis set. Bond distances are given in Å and angles, in deg.

affinity is followed by an unexpected decrease of the BDE. The deviation of the two sets of values related to $[Cu-ON_2]^+$ and $[Cu-N_2O]^+$ from the correlation line may originate from a different behavior of N_2O with copper, which shows that it can be inadequate to approximate a copper cation as a proton.

$[Cu-L]^{2+}$. The three methods have also been used to calculate BDEs for Cu^{2+} complexes containing NH_3, H_2O, CO, N_2O, NO_2, O_2, and N_2 (Figure 4). The BDEs associated with the $[Cu-L]^{2+}$ complexes are much higher than those associated with the $[Cu-L]^+$. As already observed for $[Cu-L]^+$ complexes, DFT methods lead to larger BDEs for $[Cu-L]^{2+}$, BP86 values being larger than B3LYP ones, and less bonded with MP2. The $[Cu-L]^{2+}$ BDE order (previously defined as an order of increasing bond dissociation strength for the whole ligands) is very different from the BDE order of $[Cu-L]^+$ complexes, the differences being related to the entities containing NO, NO_2, CO, and O bonded N_2O. The different methods lead also to larger deviations for the $[Cu-L]^{2+}$ than for the $[Cu-L]^+$ complexes. These differences in BDE originate partly from differences in geometries for the $[Cu-L]^{2+}$ structures, as illustrated in Figure 4. The symmetry calculated with the three methods was the same for every $[Cu-L]^{2+}$ complex except $[Cu-H_2O]^{2+}$, $[Cu-N_2O]^{2+}$, and $[Cu-N_2]^{2+}$. For $[Cu-H_2O]^{2+}$, geometries related with different symmetries and different electronic ground states were found, depending on the methods, as has been recently shown.[21] Indeed, a more stable C_s structure was calculated using DFT methods whereas a more stable C_{2v}

TABLE 2: BDEs of $[Cu-L]^{2+}$ Complexes

		BDEs (kcal/mol)					
$[Cu-L]^{2+}$	symmetry	BP86/BI	B3LYP/ BI	MP2/BI (ROMP2/BI)	CCSD(T)/BI	exp	theo
							131.1 MP2[33,f]
							151.1 B3LYP[20,e]
$[Cu-NH_3]^{2+}$	C_{3v}	164.8	150.7	121.3	126.8[e]	133.4 CSMS[a,5]	126.9 CCSD(T)[20,e]
$[Cu-CO]^{2+}$	$C_{\infty v}$	103.5	88.9	71.7(71.5)	71.4[e]		
							99.7 MP2[33,f]
							115.8 B3LYP[20,e]
							CCSD(T) 94[20,e]
$[Cu-H_2O]^{2+}$	C_s	129.0	114.4	91.5[a]	93.7[a,e]	75.9 CSMS[5]	CCSD(T) 103.8[21,e]
$[Cu-NO]^{2+}$	$C_{\infty v}$	163.7	123.5[b,e]	124.9[b,e]	105.2[b,e]		
$[Cu-N_2O]^{2+}$	C_s	128.1	107.9	65.3[d,e]			
$[Cu-N_2]^{2+}$	$C_{\infty v}$	86.4	70.8	49.9[c] (53.5)	56.2[e]		
$[Cu-NO_2]^{2+}$	C_s	140.7[b]	117.8[b]				
$[Cu-ON_2]^{2+}$	C_s	116.9	101.8	55.1[e]			
$[Cu-O_2]^{2+}$	C_s[g]	61.5[e]	53.6[e]	21.6[e]	61.6[e]		

[a] CSMS = charge-stripping mass spectrometry. [a] C_{2v} symmetry. [b] B3LYP/BII. [c] C_s symmetry. [d] $C_{\infty v}$ symmetry. [e] ZPE correction and no BSSE correction. [f] No ZPE and no BSSE correction. [g] Multiplicity is 4.

structure was obtained with Hartree−Fock methods, MP2, and CCSD(T). For $[Cu-N_2O]^{2+}$, MP2 leads to a linear structure whereas a bent structure was obtained with BP86 and B3LYP. The structure we calculated using the B1LYP functional leads to the expected linear structure for $[Cu-N_2O]^{2+}$. On the other hand, for $[Cu-N_2]^{2+}$, MP2 leads to a bent structure whereas a linear structure is obtained using the BP86, B3LYP, ROMP2, and CCSD(T) methods (Table 2, Figure 4). For L being NO or NO_2, the calculations were very dependent on the choice of the basis set. MP2 associated with the BI basis does not converge for $[Cu-NO]^{2+}$ nor for $[Cu-NO_2]^{2+}$. Using the BII basis, a minimum was found for $[Cu-NO]^{2+}$ but not for $[Cu-NO_2]^{2+}$. The B3LYP method associated with the BI basis also does not provide a stable $[Cu-NO]^{2+}$ nor a stable $[Cu-NO_2]^{2+}$. However, changing the ligand and/or the metal basis set modifies the result: using the BII basis, a double-ξ 6-31G(d) basis set, instead of the triple-ξ Wachters basis set for copper, leads to find minima on the potential energy surface for $[Cu-NO]^{2+}$ and $[Cu-NO_2]^{2+}$ (Table 2). However, a double-ξ 6-31G(d) basis is most probably not the most adequate basis set for the description of $[Cu-NO]^{2+}$ and $[Cu-NO_2]^{2+}$, because from theory, the best results should be obtained by increasing the size of the basis set.

In addition to the formation of Cu^{2+} and L, $[Cu-L]^{2+}$ dissociates into Cu^+ and L^+. The fragmentation energies of $[Cu-L]^{2+}$ are reported in Table 3 for the two channels: the straighforward dissociation leading to the formation of Cu^{2+} and the neutral ligand and the dissociation into Cu^+ and L^+ cations occurring through a dissociation barrier. Except for the copper−ligand distances, the structures of the $[Cu-L]^{2+}$ complexes and of the corresponding transition states are comparable. As calculated Table 3, the barriers exist for all the complexes, including $[Cu-N_2O]^{2+}$, which confirms the existence of these complexes.

To our knowledge, the only experimental BDEs available for Cu^{2+} involve H_2O and NH_3. The comparison of our calculated values with those obtained by experiments[5] indicate that among the three methods, MP2 calculations would give the best results, with $150.7_{B3LYP} > 133.4\ exp_{NRMS} > 121.3_{MP2}$ kcal/mol for $[Cu-NH_3]^{2+}$ and $114.4_{B3LYP} > 91.5_{MP2} > 75.9_{NRMS}$ kcal/mol for $[Cu-H_2O]^{2+}$. The differences between the methods for the $[Cu-NH_3]^{2+}$ and $[Cu-H_2O]^{2+}$ BDEs are much larger than those calculated for $[Cu-NH_3]^+$ and $[Cu-H_2O]^+$. The validation of the methods is, however, difficult, due to the lack of available experimental results. Furthermore, theses experimental thermodynamic values for the Cu^{2+} compounds should be taken as a crude estimate because they are provided by coupling experiments, charge stripping mass spectrometry and by gas-phase measurements, increasing the errors.

In contrast to $[Cu-NH_3]^{2+}$ the experimental value reported for $[Cu-H_2O]^{2+}$ is very low in comparison to the CCSD(T) value (Table 2). Such a result was not expected because the CCSD(T) led to much smaller differences for all the studied complexes, including the Cu^+ complexes. The analysis of the absolute energy values involved in the BDE calculations showed that most of the differences between the methods are provided by the $[Cu-L]^{2+}$ and Cu^{2+} relative energies and only slightly by the ligands. Comparison of the experimental ionization energies of Cu^+ ($IE_{exp} = 20.30$ eV)[22] with the calculated values ($IE_{BP86} = 20.82$ eV, $IE_{B3LYP} = 20.40$ eV, $IE_{MP2} = 19.84$ eV) illustrates the large BDE differences between the methods. Hence, the differences between the BDE of $[Cu-L]^{2+}$ using the three methods originate essentially from the differences between the multiplet energies of isolated Cu^{2+}, illustrating the difficulty of modeling isolated transition metal ions.[23] The increase of admixture of the Hartree−Fock exchange to density functional was proposed to adjust the self-interaction correction.[24] This would lead to a decrease in BDE values from BP86 to B3LYP. However, as will be shown below (see section $[Cu(NH_3)_4]^+$ and $[Cu(NH_3)_4]^{2+}$), the decrease of BDE values from BP86 to B3LYP is very small for higher coordinated copper for which the discrepancies between the methods are negligible.

We should point out that the different methodologies do not lead always to the same symmetries for the structures of $[Cu-L]^{2+}$. However, as has been recently shown in the case of $[Cu-H_2O]^{2+}$,[24] the increase of admixture of the Hartree−Fock exchange to density functional with the B1LYP functional led to the same C_∞ symmetry for $[Cu-N_2O]^{2+}$ as calculated with post-Hartree−Fock methods. Based on our results, MP2 calculation leads to particular problems. For $[Cu-N_2]^{2+}$ a wrong bent geometry was calculated with MP2 in contrast to a linear structure obtained with ROMP2 and other methods (Table 2), which may originate from spin contamination. In contrast to Cu^+, the use of ROMP2 does not lead always to an important increase of the BDE values calculated with MP2. Concerning $[Cu-NO_2]^{2+}$, no stable structure was calculated despite a strong interaction calculated with DFT. The difficulty in finding a minimum may result from the fact that the right set of orbitals was not found.[8] The choice of the basis set seems also to be crucial because for the close shell $[Cu-NO]^{2+}$, changing the basis set from BI to BII led to a stable structure. A comparable influence of the basis was observed for B3LYP because stable

TABLE 3: Calculated Structure Parameters and ΔH_{OK} of $[Cu-L]^{2+}$ Complexes, Their Transition States, and Products and Experimental Ionization Energies of L

Cu−A−B−C B3LYP/BI	Cu−A, Å	A−B, Å	B−C, Å	Cu−A−B, deg	A−B−C, deg	ΔH_{OK} (kcal/mol)	IE, eV
$[CuN_2]^{2+}$	1.93	1.09				0.0	
TS $[Cu\text{--}N_2]^{2+}$	3.06	1.10				17.9	$N_2 = 15.58$
$Cu^+ + N_2^+$	∞	1.10				−30.2	
$Cu^{2+} + N_2$	∞	1.09				72.7	
$[CuN_2O]^{2+}$	1.94	1.14	1.15	166.4	176.3	0.0	$N_2O = 12.89$
TS $[Cu\text{- -}N_2O]^{2+}$	2.68	1.14	1.17	179.8	180.0	6.6	
$Cu^+ + N_2O^+$	∞	1.14	1.19		180.0	−61.2	
$Cu^{2+} + N_2O$	∞	1.12	1.19		180.0	109.4	
$[CuON_2]^{2+}$	1.94	1.23	1.11	139.3	174.2	0.0	
TS $[Cu\text{- -}ON_2]^{2+}$	2.50	1.21	1.12	154.9	177.5	3.7	$N_2O = 12.89$
$Cu^+ + N_2O^+$	∞	1.14	1.19		180.0	−67.8	
$Cu^{2+} + N_2O$	∞	1.12	1.19		180.0	102.8	
$[CuNH_3]^{2+}$	1.93	1.03		109.8	109.2	0.0	
TS $[Cu\text{- -}NH_3]^{2+}$	2.74	1.03		101.5	116.2	11.9	$NH_3 = 10.07$
$Cu^+ + NH_3^+$	∞	1.02			120.0	−79.8	
$Cu^{2+} + NH_3$	∞	1.01			107.2	153.6	
$[CuOH_2]^{2+}$	1.89	0.99		122.0	107.2	0.0	
TS $[Cu\text{- -}OH_2]^{2+}$	2.76	0.99		125.5	106.6	11.7	$H_2O = 12.62$
$Cu^+ + H_2O^+$	∞	1.00			109.6	−60.1	
$Cu^{2+} + H_2O$	∞	0.96			105.1	116.6	
$[CuCO]^{2+}$	1.99	1.11		180.0		0.0	
TS $[Cu\text{- -}CO]^{2+}$	3.11	1.11		180.0		20.1	$CO = 14.01$
$Cu^+ + CO^+$	∞	1.11				−50.7	
$Cu^{2+} + CO$	∞	1.13				91.1	
$[CuNO]^{2+\,a}$	1.78	1.08		180.0		0.0	
TS $[CuNO]^{2+\,a}$	2.79	1.07		180.0		16.0	$NO = 9.26$
$Cu^+ + NO^{+\,a}$	∞	1.06				−57.0	
$Cu^{2+} + NO^a$	∞	1.15				125.2	
$[CuO_2]^{2+}$	1.93	1.23		134.8		0.0	$O_2 = 12.07$
TS $[Cu\ O_2]^{2+}$	2.51	1.17		134.1		10.4	
$Cu^+ + O_2^+$		1.11				−124.4	
$Cu^{2+} + O_2$		1.21				54.0	
$[CuNO_2]^{2+\,a}$	1.92	1.14	1.12	160.4	179.4	0.0	$NO_2 = 9.90$
TS $[Cu\ NO_2]^{2+\,a}$	3.79	1.15	1.13	164.1	180.0	4.4	
$Cu^+ + NO_2^{+\,a}$		1.12			180.0	−60.1	
$Cu^{2+} + NO_2^a$		1.19			134.3	118.7	

[a] B3LYP/BII.

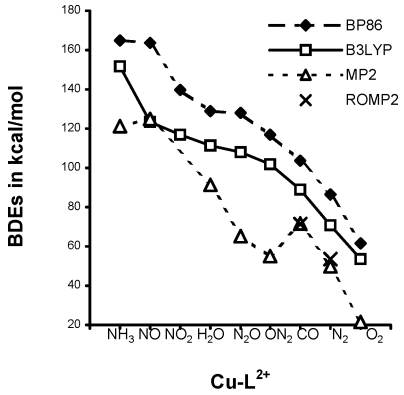

Figure 5. Calculated Bond Dissociation Energies of $[Cu-L]^{2+}$ using BP86, B3LYP, MP2, and ROMP2 and the BI basis set in kcal/mol.

structures were found for $[Cu-NO]^{2+}$ and $[Cu-NO_2]^{2+}$ using the BII basis set only. The basis set effect between BI and BII can be explained by a too large charge transfer from NO to Cu when the basis on copper is more extended (BI), favoring the charge-separation between NO^+ (or NO_2) and Cu^+. In contrast, the BII basis involving the smaller double-ξ 6-31G basis on copper would stabilize the complexes $[Cu-NO]^{2+}$ and $[Cu-NO_2]^{2+}$.

Despite the strong differences among the methods for Cu^{2+} systems, Figure 5 shows that the DFT curves have similar shapes. Indeed, the BDE order for $[Cu-L]^{2+}$ ($[Cu-NH_3]^{2+}$ > $[Cu-NO]^{2+}$ > $[Cu-NO_2]^{2+}$ > $[Cu-H_2O]^{2+}$ > $[Cu-N_2O]^{2+}$ > $[Cu-ON_2]^{2+}$ > $[Cu-CO]^{2+}$ > $[Cu-N_2]^{2+}$ > $[Cu-O_2]^{2+}$) is the same for BP86 and B3LYP in contrast to $[Cu-L]^+$. Considering the three methods, the differences in the binding abilities of NH_3, H_2O, CO, and N_2 ligands are comparable, whereas they were very different for Cu^+. For instance, going from H_2O to NH_3, the BDEs increase is comparable whatever are the methods used for the Cu^{2+} complexes (73% using BP86 and 79% using MP2), whereas for the Cu^+ complexes the BDEs increase is different (64% using BP86 and 78% using MP2). Larger differences between the methods were calculated for N_2O and O_2.

The analysis of the bonding of Cu^{2+} with molecules showed that a charge transfer from the ligand to Cu^{2+} has an important contribution into the interaction, illustrating the larger electron redistribution in the adduct, related partly with the d hole of Cu^{2+}.[24−27] However, depending on the ligand, the charge transfer in $[Cu-L]^{2+}$ can facilitate the formation of Cu^+ and L^+.[28] As a general behavior, the straighforward dissociation is very endothermic whereas the dissociation into Cu^+ and L^+ is exothermic. It is generally admitted that a large difference between the ionization energies of Cu^+ (20.3 eV) and L is associated with a higher charge transfer and then an easier charge separation process. In such a condition, the $[Cu-L]^{2+}$ would dissociate in Cu^+ and L^+ without an energy minimum in the ground state. However, as reported in Table 3, the calculations based on ΔH at 0 K showed that a lower IE of the ligand is not associated with a lower energy dissociation barrier of the complex. These results demonstrate that using the

TABLE 4: Sequential BDEs of $[Cu-(NH_3)_{x=1-4}^+]$ and $[Cu-(NH_3)_{x=1-4}^{2+}]$ Complexes at 298 K

		sequential BDEs (kcal/mol) at 298 K			
		$x=1$	$x=2$	$x=3$	$x=4$
$[Cu-(NH_3)_x]^+$	BP86/BIII	63.3	58.6	7.9	4.1
	PBE/BIII	64.6	59.5	9.2	5.4
	B3LYP/BIII	57.8	54.9	8.2	3.6
	B3LYP/BI	53.9	51.4	8.3	5.4
	MP2/BIII	46.7	50.4	6.5	1.1
	exp[12]	56.7	59.3	11.0	10.8
$[Cu-(NH_3)_x]^{2+}$	BP86/BIII	168.5	103.6	67.9	42.8
	PBE/BIII	170.8	104.5	68.9	44.3
	B3LYP/BIII	152.2	102.2	64.2	42.3
	B3LYP/BI	151.5	98.0	60.5	38.6
	MP2/BIII	128.4	101.0	56.7	40.5

ionization energy of the ligand as an indicator did not allow us to anticipate the stability of the complexes.

The study of $[Cu-L]^{2+}$ complexes showed that the different methods, BP86, B3LYP, and MP2, led to very different BDE values. For $[Cu-NH_3]^{2+}$, both B3LYP and MP2 can be considered as the methods giving the most reliable results. On the contrary, for $[Cu-H_2O]^{2+}$, no method is giving values close to experimental results, not even CCSD(T). Considering the whole calculated values, these results suggested that the B3LYP gave the most reliable BDE values among the BP86, B3LYP, and MP2 methods.

$[Cu-(NH_3)_4]^+$ and $[Cu-(NH_3)_4]^{2+}$. When transition metal ions are involved in biomolecules or in organometallic materials, they are most generally coordinated to at least three ligands. Then, it is useful to study higher copper coordinations comparing the different methods.

We have studied the sequential metal−ammonia BDEs at 298 K involving Cu^+ and Cu^{2+} with one to four ligands (Table 4, Figure 6). The BDEs are reported at 298 K because the experimental BDEs given in the litterature contain temperature corrections to give the BDEs at 298 K. A labeled BIII basis set containing double-ξ basis set on N and H atoms was chosen for these larger systems instead of the BI basis set containing triple-ξ basis set on N and H atoms, because it is the most generally used basis set for large systems. Nevertheless, B3LYP/BI values are also reported to show the influence of the basis set upon the results. The sequential binding energy dissociation is defined as the difference between the energy of $[Cu-(NH_3)_{x-1}]^{+/2+}$ + NH_3 and $[Cu(NH_3)_x]^{+/2+}$, i.e., $[H[Cu-(NH_3)_{x-1}]^{+/2+} + H(NH_3) - H[Cu(NH_3)_x]^{+/2+}]$. In the case of Cu^+, the experimental BDEs is slightly increasing from $x = 1$ to $x = 2$ and then decreasing from $x = 2$ to $x = 3$ and $x = 4$. The increase of the BDEs associated with the loss of NH_3 from $[Cu(NH_3)]^+$ to $[Cu(NH_3)_2]^+$ has been attributed to the ability of the transition metal to reduce the metal−ligand repulsion by a sdσ hybridization.[29] The increase of BDE from $x = 1$ to $x = 2$ is observed only using MP2, but not with B3LYP nor with the BP86 and PBE functionals. A comparable result was reported for Cu^+ with acetone using MP2 and B3LYP calculations.[30] These results would indicate that DFT modeling underestimates the sdσ hybridization. More generally, it is difficult to calculate accurately the BDE increase between $x = 1$ to $x = 2$. Indeed, using high correlated MCPF calculations[12] the reported increase of BDE from $x = 1$ to $x = 2$ is too small (less than 0.5 kcal/mol), whereas using MP2, it is too large (3.7 kcal/mol) in comparison to the experimental value (2.6 kcal/mol). However, considering all the BDE values using different methods, the reported curves in Figure 6 agree approximately with the experimental curve.

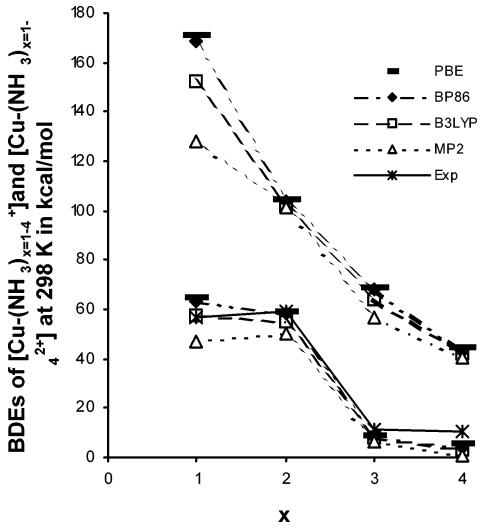

Figure 6. Calculated and experimental Sequential Bond Dissociation Energies of $[Cu-(NH_3)_{x=1-4}]^+$ and $[Cu-(NH_3)_{x=1-4}]^{2+}$ complexes in kcal/mol at 298 K.

The good agreement of B3LYP with experiment for the monoligated complex $[Cu-NH_3]^+$, which gave us confidence in the accuracy of this B3LYP method, is also observed for the four coordinated complex, but the good agreement is also obtained with the other methods. Indeed, the analysis of the $[Cu-(NH_3)_{x=4}]^+$ sequential BDE shows that the differences between the methods decrease from $x = 1$ to $x = 4$. Even if the differences between the BDE values are small when $x = 4$, the best BDE value was obtained with the DFT PBE functional. In the case of Cu^{2+} the BDE decrease is nearly linear, but the slope is lower for MP2 than for BP86. The various methods lead to different first ammonia BDEs whereas they provide closer or almost similar second, third, and fourth ammonia BDEs. Based on a percentage, the results show that the differences between the values are less than 5% for $x = 2$ to $x = 4$ for Cu^{2+}, whereas they are much higher for Cu^+. However, for both Cu^+ and Cu^{2+}, the BDE values for the fourth ammonia BDEs ($x = 4$) calculated with the various methodologies are very comparable, with maximum differences of 3.8 kcal/mol for Cu^{2+} and 4.3 kcal/mol for Cu^+. This result indicates that the BDE values for the loss of one ligand do not depend on the methods, when copper cation (Cu^+ and Cu^{2+}) is four coordinated.

In addition to the loss of NH_3, the charge separation reaction of $[Cu-(NH_3)_4]^{2+}$ into $[Cu-(NH_3)_3]^+$ and NH_3^+ was studied (Table 5). In comparison to the monoligated copper (Table 3), for $[Cu-(NH_3)_4]^{2+}$ the energy difference is smaller between the two different processes, i.e., versus the formation of the dication and NH_3 and the charge separation mechanism leading to the formation of two cations (Table 5). The reaction of charge separation of $[Cu-(NH_3)_4]^{2+}$ is the most favorable process because it is exothermic whereas the loss of a neutral fragment is endothermic, as was calculated for $[Cu-NH_3]^{2+}$. Then, decreasing the Cu oxidation state appears to be the most favorable process. To take into account also the entropic term, the Gibbs energies were evaluated for the reactions of decomposition of $[Cu-NH_3)_4]^{2+}$ (Table 5). Whereas enthalpy energies of $[Cu-(NH_3)_3]^{2+}$ do not depend on the methods, calculated entropic terms are much more sensitive. Strong differences are obtained for the enthalpy and Gibbs energy values associated with the formation of $[Cu-(NH_3)_3]^+$ and NH_3^+, especially with the MP2 method. These results show that when there is a change of the oxidation state during the reaction, the enthalpy and Gibbs energy values depend on the calculation methods. Then, this

TABLE 5: ΔH_{298K} and ΔG_{298K} (kcal/mol) for the Loss of NH_3 and NH_3^+ from $[Cu-(NH_3)_4]^{2+}$, Labeled ($2^+ \rightarrow 2^+ + 0$) and ($2^+ \rightarrow {}^+ + {}^+$) Respectively

	B3LYP/BI	B3LYP/BIII	BP86/BIII	PBE/BIII	MP2/BIII
$\Delta H_{298K}(2^+ \rightarrow 2^+ + 0)$	38.6	42.3	42.8	44.3	40.5
$\Delta H_{298K}(2^+ \rightarrow {}^+ + {}^+)$	−11.3	−3.8	−1.2	0.6	−22.2
ΔG_{298K} $(2^+ \rightarrow 2^+ + 0)$	31.5	27.6	32.5	34.5	29.8
ΔG_{298K} $(2^+ \rightarrow {}^+ + {}^+)$	−17.0	−22.3	−13.2	−10.8	−34.5

study showed that the choice of the methodoloy is less decisive for complexes involving a high coordination of the metal, however, the oxidation state should be the same along the studied reaction process.

In a more general sense, this study shows that monoligated and high coordinated copper have large differences in BDE values and emphasizes that modeling the chemical reactions of transition metal complexes needs to know what is the coordination of the metal.

Conclusion

The comparative study of the Bond Dissociation Energies (BDEs) of $[Cu-L_{x=1,4}]^+$ and $[Cu-L_{x=1,4}]^{2+}$ complexes containing NH_3, H_2O, CO, NO, N_2O, NO_2, N_2, and O_2 ligands using DFT based and post-Hartree−Fock methodologies showed that:

•Based on monoligated copper results, the B3LYP functional gave the most reliable binding energy order and values for either Cu^+ and Cu^{2+}. In contrast, BP86 led to overestimated BDEs and MP2 to underestimated BDEs, both leading also to wrong BDE orders for some ligands. For $[Cu-H_2O]^{2+}$ and $[Cu-N_2O]^{2+}$, BP86 and B3LYP led to wrong symmetries for the ground state structures. For these two complexes, the right symmetry was obtained using the B1LYP functionnal. In some cases, MP2 led to abnormal results, which can be partly explained by spin contamination contribution. The lack of accuracy of MP2 is confirmed also by comparing the results obtained with the high correlated CCSD(T) method, which are generally higher using CCSD(T) than MP2. The large differences between the BDEs of $[Cu-L]^{2+}$ originate mostly from the differences in the Cu^{2+} energy values which are very dependent on the methods used.

•For complexes with a higher coordination of the metal, illustrated with the $[Cu-(NH_3)_{x=4}]^+$ and $[Cu-(NH_3)_{x=4}]^{2+}$ complexes, the sequential BDEs showed that the differences between the methods became smaller from $x = 1$ to $x = 4$. Going from $x = 1$ to $x = 2$, i.e., when the Cu^+ complex lost its second ligand, the results differed with the methods. Our results showed that the phenomenon of increase of the BDEs observed experimentally is reproduced only with MP2 method. However, the best BDE values were obtained with the B3LYP for $x = 1$ and with the BP86 and PBE for $x = 2$. Our calculations did not lead to significant changes of the values upon changing the PB86 functional to the PBE functional. When the coordination is 3 or 4, which is the most frequently met coordination in chemistry and biology, whatever the methods, the BDEs are almost the same for Cu^+ as well as for Cu^{2+}. The choice of the method is then less crucial for higher coordinated copper. However, our study showed that the same values are obtained only when the oxidation state does not change upon the reaction. In fact, when the $[Cu-(NH_3)_4]^{2+}$ dissociated into $[Cu-(NH_3)_3]^+$ and NH_3^+, we showed that the BDE values depend strongly on the method.

Acknowledgment. We acknowledge useful discussion with Dr. Sourav Pal who was visiting our Laboratory on the collaboration project sponsored by Indo-French Centre for the Promotion of Advanced Research (IFCPAR, New Delhi). These calculations were carried out on the IBM SP4 computer of the CINES (Centre Informatique National de l'Enseignement Supérieur) in Montpellier (France) and on the NEC-SX5 of the IDRIS (Institut des Ressources en Informatique Scientifique) in Orsay (France).

References and Notes

(1) Armentrout, P. B.; Kickel, B. L. *Organometallic Ion Chemistry*; Kluwer: Dordrecht, The Netherlands, 1996.
(2) Armentrout, P. B. *Int. J. Mass Spectrom.* **2003**, *227*, 289.
(3) Williams, R. J. P. *Chem. Commun. (Cambridge, United Kingdom)* **2003**, 1109.
(4) Delahay, G.; Berthomieu, D.; Goursot, A.; Coq, B. Zeolite-based catalysts for the abatement of NOX and N2O emissions from man-made activities. *Surfactant Science Series*; 2003; Vol. 108, p 1.
(5) Schroder, D.; Schwarz, H.; Wu, J.; Wesdemiotis, C. *Chem. Phys. Lett.* **2001**, *343*, 258.
(6) Luna, A.; Alcamí, M.; Mó, O.; Yañez, M. *Chem. Phys. Lett.* **2000**, *320*, 129.
(7) Ghanty, T. K.; Davidson, E. R. *Int. J. Quantum Chem.* **2000**, *77*, 291.
(8) Lynch, B. J.; Truhlar, D. G. *Chem. Phys. Lett.* **2002**, *361*, 251.
(9) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(10) McQuarrie *Statistical Mechanics*; Harper Collins Publishers Inc: New York, 1976.
(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; J. A. Montgomery, J.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; G. Liu; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; E. S. Replogle, a. J. A. P. *Gaussian98*, revision A.9 ed.; Gaussian, Inc.: Pittsburgh, PA, 1998.
(12) Walter, D.; Armentrout, P. B. *J. Am. Chem. Soc.* **1998**, *120*, 3176.
(13) Hrusak, J.; Koch, W.; Schwarz, H. *J. Chem. Phys.* **1994**, *101*, 3898.
(14) Koszinowski, K.; Schroeder, D.; Schwarz, H.; Holthausen, M. C.; Sauer, J.; Koizumi, H.; Armentrout, P. B. *Inorg. Chem.* **2002**, *41*, 5882.
(15) Morgantini, P. Y.; Weber, J. *THEOCHEM* **1988**, *43*, 247.
(16) Zhou, M.; Andrews, L.; Bauschlicher, C. W., Jr. *Chem. Rev.* **2001**, *101*, 1931.
(17) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2296.
(18) Luna, A. A. B.; Morizur, J. P.; Tortajada, J.; Mó, O.; Yañez, M. *J. Phys. Chem. A* **2000**, *104*, 3132.
(19) Hunter, E. P. L., S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.
(20) El-Nahas, A. M.; Hirao, K. *J. Phys. Chem. A* **2000**, *104*, 138.
(21) Poater, J.; Sola, M.; Rimola, A.; Rodriguez-Santiago, L.; Sodupe, M. *J. Phys. Chem. A* **2004**, *108*, 6072.
(22) Moore, C. E. *Ionization potentials and ionization limits derived from the analyses of optical spectra*; U.S. Natl. Bur. Stand: Washington, DC, 1970; Vol. Circ. No. 34.
(23) Mineva, T.; Goursot, A.; Daul, C. *Chem. Phys. Lett.* **2001**, *350*, 147.
(24) Bertrán, J.; Rodríguez-Santiago, L.; Sodupe, M. *J. Phys. Chem. B* **1999**, *103*, 2310.
(25) Berthomieu, D.; Krishnamurty, S.; Coq, B.; Delahay, G.; Goursot, A. *J. Phys. Chem. B* **2001**, *105*, 1149.
(26) Berthomieu, D.; Ducéré, J.-M.; Goursot, A. *J. Phys. Chem. B* **2002**, *106*, 7483.
(27) Noguera, M.; Bertrán, J.; Sodupe, M. *J. Phys. Chem. A* **2004**, *108*, 333.
(28) El-Nahas, A. M.; Tajima, N.; Hirao, K. *Chem. Phys. Lett.* **2000**, *318*, 333.
(29) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H. *J. Chem. Phys.* **1991**, *94*, 2068.
(30) Chu, Y.; Yang, Z.; Rodgers, M. T. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 453.
(31) Clemmer, D. E.; Armentrout, P. B. *J. Phys. Chem.* **1991**, *95*, 3084.

(32) Langhoff, S. R.; Bauschlicher, C. W., Jr.; Partridge, H.; Sodupe, M. *J. Phys. Chem.* **1991**, *95*, 10677.
(33) Magnusson, E.; Moriarty, N. W. *Inorg. Chem.* **1996**, *35*, 5711.
(34) Luna, A.; Amekraz, B.; Tortajada, J. *Chem. Phys. Lett.* **1997**, *266*, 31.
(35) Meyer, F.; Chen, Y.-M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 4071.
(36) Barnes, L. A.; Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1990**, *93*, 609.
(37) Dalleska, N. F.; Honma, K.; Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 3519.
(38) Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1990**, *92*, 1876.
(39) Thomas, J. L. C.; Bauschlicher, C. W., Jr.; Hall, M. B. *J. Phys. Chem. A* **1997**, *101*, 8530.
(40) Delabie, A.; Pierloot, K. *J. Phys. Chem. A* **2002**, *106*, 5679.
(41) Rodgers, M. T.; Walker, B.; Armentrout, P. B. *Int. J. Mass Spectrom.* **1999**, *182/183*, 99.