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Theoretical description of copper Cu(I)/Cu(II) complexes in mixed ammine-aqua environment. DFT and ab initio quantum chemical study

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Abstract

This work is devoted to investigate the interactions of the Cu(I)/Cu(II) cation with variable ammonia–water ligand field by the quantum chemical approach. For that purpose, the optimization of the $[Cu(NH_3)_m(H_2O)_n]^{2+/+}$ complexes (where n varies from 0 to 4 or 6 and $m + n = 4$ or 6) has been performed at the DFT/6-31+G(d) level of theory in conjunction with the B3PW91 hybrid functional. Based on the results of the single-point B3LYP/6-311++G(2df,2pd) calculations, the stabilization energies were determined. The two-coordinated copper(I) complexes appeared to be the most stable compounds with the remaining water or ammonia molecules in the second solvation shell. In the case of the Cu(II) systems, four-coordinated complexes were found to be the most stable. In order to examine and explain bonding characteristics, Morokuma interaction energy decomposition (for selected Cu^+ complexes) and Natural Population Analysis for all systems were performed. It was found that the most stable structures correlate with the highest donation effects. Therefore, more polarizable ammonia molecules exhibit higher donation than water and thus make stronger bonds to copper. This can be demonstrated by the fact that the NH_3 molecule always tries to occupy the first solvation shell in mixed ammine-aqua complexes.

Keywords: DFT calculations; Copper complexes

1. Introduction

Copper is essential for an "au naturel" occurrence of many processes in bioorganisms. Hence, there is a huge number of works investigating biological activity of the copper ions and their interactions using both experimental and theoretical approaches. Copper cation interactions with amino acids were investigated in studies [1–9] using various computational approaches. Experimental measurements, which were published, e.g., in [10–12] initiated some of these studies and were basically confirmed or some of their conclusions were explained by above-mentioned theoretical works. Very prosperous is the exploration of the so-called blue proteins, a group of electron transfer systems characterized by a bright blue color, a narrow hyperfine splitting in the electronic spin resonance spectra and especially high reduction potential. Their active centers are formed by a redox copper Cu(I)/Cu(II) cation coordinated usually with cysteine and histidine side chains. The coordination sphere is typically completed by the methionine side chain. A comparison of the geometry arrangements in reduced and oxidized protein centers were studied by Olsson's group [13–16]. The authors have pointed to large similarity of both forms. This structural feature is also discussed by Randall et al. [17,18] and in some other works [19–21]. These results can be compared with, e.g., pump and probe spectroscopy [22] or

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measurements of resonance Raman intensities [23]. Finally, copper plays an important role in many other enzymatic processes [24] – e.g. cytochrome *c* oxidase, lactase [25], Cu,Zn-superoxidase dismutase, ceruloplasmin, diammineoxidase, azurin [26] and indophenol-oxidase or tyrosinase [27].

Other interesting topics deal with adducts of copper and DNA/RNA bases studied with ab initio techniques [28–31], for which one can find many experimental evidences [32–37].

Many studies are devoted to examination of simple models in order to determine electronic properties of various copper complexes. The Cu cations in water or ammonium solution are subjects investigated via static [38–40] and dynamic [41–44] approaches or methods combining both tools [45–48]. Stable two-coordinated Cu(II) complexes were observed experimentally in gas phase [49]. On the contrary, the high-coordination was treated as preferred in solution or in solid state [50]. Copper force-field parameters were subject of several studies [51–53] since the requirement of large-scale MM/MD molecular simulations is very urgent in biodisciplines. The SIBFA method presented in paper of Gresh [54] is one of the interesting and promising approaches in this field. Some of Cu(I) and Cu(II) complexes were successfully solved using this technique [55,56].

The aim of this study is to find energetic and electronic relations between the structures of Cu(I)/Cu(II) cations interacting with variable ammonia–water environment. In the present paper, a thorough comparison with similar results found in the literature [2,3,41–43,45–47,50,57] was also done. Finally, it should be mentioned that this work complements our previous study of copper hydration [64].

2. Computational details

Since the investigated $[Cu(NH_3)_m(H_2O)_n]^+$ complexes, where n varies from 0 to 4 or 6 and $m + n = 4$ or 6 are the closed shell systems, singlet electronic configuration represents the ground state of these compounds. Detailed geometry search was performed. Several local minima were obtained. Similar situation was already described, e.g., in studies [39,45]. In this work, only the most stable various-coordinated structures are presented. The optimized geometries were obtained at the DFT level of theory using the B3PW91 functional. In comparison with B3LYP, structures and frequency properties obtained using the B3PW91 functional are slightly better [58–61]. All the low-lying minima were confirmed by the frequency analysis. Standard 6-31+G(d) basis set with diffusion functions was used for the ligand description. Electrons on the copper atom were described by Christiansen averaged relativistic effective pseudopotential (AREP) [62]. Basis set of pseudoorbitals was extended by diffuse and polarization functions ($\alpha_s = 0.025$, $\alpha_p = 0.35$, $\alpha_d = 0.07$ and $\alpha_f = 3.75$) in correspondence with 6-31+G(d) set [63].

The open shell Cu^{2+} cation has the $3d^9$ electron configuration. Consequently, the ground states of $[Cu(NH_3)_m(H_2O)_n]^{2+}$ complexes were considered as doublets. Besides a few systems, computational procedure in 6-31+G(d) basis came to wrong orbital occupation or failed completely when general guess was applied. Therefore at first, an appropriate wavefunction was constructed in minimal basis set using Restricted Open Shell Hartree-Fock (ROHF) procedure, and used as a guess for calculation with augmented basis set ROHF/6-31+G(d). Then geometry optimization at the unrestricted Hartree-Fock (UHF) level was performed. Finally, the UHF structure was re-optimized with the B3PW91 functional.

Analysis of the energy characteristics and the charge distribution was performed on the most stable structures using B3LYP functional. Extended basis set 6-311++G(2df,2pd) was utilized for the oxygen, nitrogen and hydrogen atoms. Basis set on the Cu atom was enlarged accordingly by s, p, d diffuse functions and by 2f, 1g polarization functions ($\alpha_f = 4.97$, 1.30 and $\alpha_g = 3.28$) in a consistent way [64]. The stabilization energies with the basis set superposition error corrections (BSSE) and deformation energies [65] were determined according to equation:

$$\Delta E^{\mathrm{Stab}} = -\left(E_{\mathrm{complex}} - \sum E_{\mathrm{monomer}} - \sum E^{\mathrm{deform}}\right), \tag{1}$$

where E_{complex} represents the total energy of a whole complex and E_{monomer} labels the energy of the individual parts computed with basis functions on the ghost atoms from the rest of the system. Besides the ΔE^{stab} energies, coordination ($\Delta E^{\mathrm{coord}}$) and sterically corrected stabilization (ΔE^{stex}) energies were computed in selected cases, as well. The coordination energy was established especially for the Cu(I) systems where ligand molecules often escaped to second hydration shell. For calculation of coordination energy, only directly bonded ligands were considered in Eq. (1) using the optimized geometry of a whole complex. Calculating ΔE^{stex}, all the interacting molecules were treated as one part simultaneously (only without the central Cu ion) in Eq. (1). These energies were determined for the Cu(II) complexes where a higher coordination is linked with increased repulsion among ligands.

For the structures with a monovalent copper, Morokuma decomposition analysis was performed using GAMESS-US program [66]. *Gaussian 98* program package [67] was used for the rest of quantum chemical calculations. For visualization of geometries, MOs, and vibrational modes, programs Molden 3.7 [68] and Molekel 4.3 [69,70] were applied.

3. Results and discussion

3.1. Cu(I) and Cu(II) structures

The objective of optimization process was to find stable Cu(I) and Cu(II) complexes with various coordination numbers, compare their stability and other properties.

For complexes with a monovalent copper, metal–ligand interaction (dative bonds together with their monopole–dipole electrostatic term) competes with a hydrogen bonding among first and second shell molecules that have very similar energy. The structures of the Cu(I) optimized complexes with 4 or 6 ammonia–water molecules are illustrated in Fig. 1.

In the two-coordinated $[Cu(NH_3)_4]^+$ complex (structure **0a**) copper makes relatively strong coordination bonds with ammine ligands in the first solvation shell (their lengths are 1.91 Å). This is also demonstrated by the increased coordination energy, Morokuma decomposition analysis, and NPA charge distribution that will be discussed below. The other two ammonia are H-bonded to the first shell where the N···H distance is about 1.9 Å.

For a less stable three-coordinated system (structure **0b**), the first coordination shell is nearly planar (bond lengths: 2.07, 2.07 and 2.00 Å) with the remaining NH_3 molecule attached to one of the ligands by the hydrogen bond (1.96 Å). The complex with 4 coordinated ammine ligands (**0c**) creates the longest Cu–N bonds (2.14 Å) with a small deviation from T_d symmetry. For all the Cu(I) complexes, copper–ligand distances are presented in Table 1. The averaged Cu–N bond dependences on the ligand type and coordination number are for a more illustrative view presented in Figs. 3(a) and (b). The shortest distances were obtained for the most stable two-coordinated structures and the longest distances for four-coordinated complexes. Both the Cu–N and Cu–O bonds are shortened with increasing number of water molecules in the first solvation shell. It is caused by stronger copper interaction with NH_3 ligands in competition with aqua ligands. The

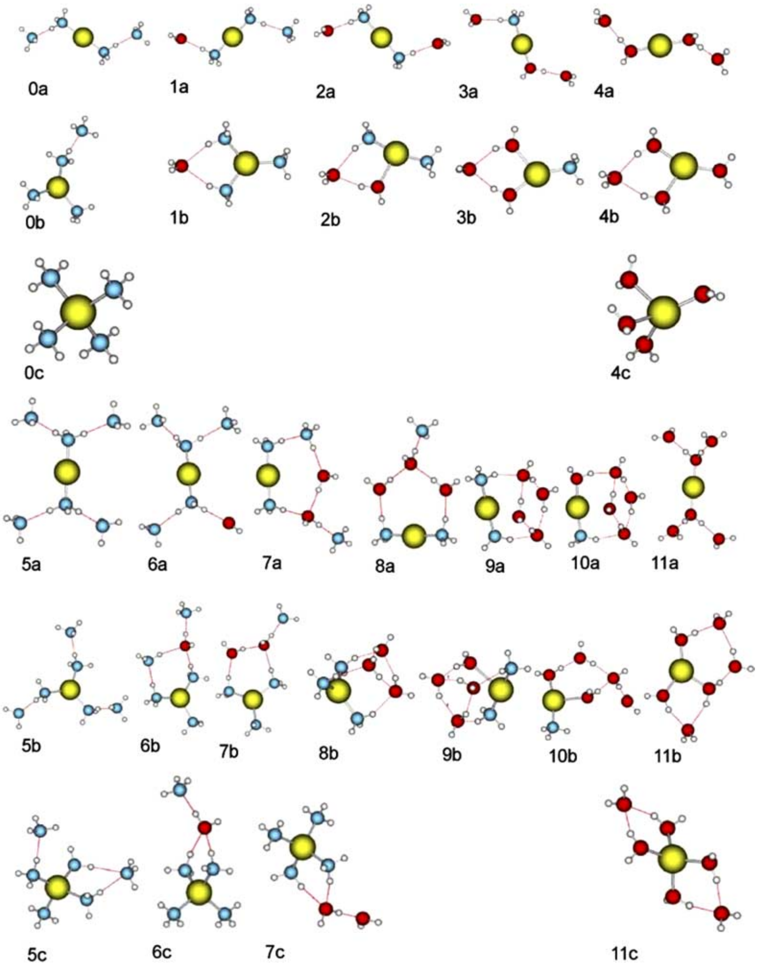

Fig. 1. (structures **0a**–**11c**) The optimized Cu(I) complexes. Systems **0**–**4** and **5**–**11** represent the $[Cu(NH_3)_m(H_2O)_n]^+$ structures, with 4 ($m + n = 4$; $n = 0$ to 4) and 6 ($m + n = 6$; $n = 0$ to 6) ammonia–water molecules, respectively. Letters a, b and c correspond to two-, three- and four-coordination.

Table 1
Copper–ligand distances (in Å) for all presented Cu(I) complexes

System	c.n.	Cu–Lig1 (Å)	Cu–Lig2 (Å)	Cu–Lig3 (Å)	Cu–Lig4 (Å)
$[Cu(lig)_4]^+$					
$[Cu(NH_3)_4]^+$	2	1.91*	1.91*		
	3	2.07*	2.00*	2.08*	
	4	2.14*	2.14*	2.14*	2.14*
$[Cu(NH_3)_3(H_2O)]^+$	2	1.91*	1.90*		
	3	2.06*	2.06*	2.01*	
$[Cu(NH_3)_2(H_2O)_2]^+$	2	1.91*	1.91*		
	3	2.35	1.94*	1.94*	
$[Cu(NH_3)(H_2O)_3]^+$	2	1.89	1.90*		
	3	1.98	2.20	1.94*	
$[Cu(H_2O)_4]^+$	2	1.88	1.88		
	3	1.97	1.98	2.14	
	4	2.00	2.09	2.21	2.26
$[Cu(lig)_6]^+$					
$[Cu(NH_3)_6]^+$	2	1.90*	1.90*		
	3	2.04*	2.04*	2.04*	
	4	2.07*	2.14*	2.16*	2.16*
$[Cu(NH_3)_5(H_2O)]^+$	2	1.90*	1.90*		
	3	2.01*	2.03*	2.10*	
	4	2.09*	2.14*	2.15*	2.16*
$[Cu(NH_3)_4(H_2O)_2]^+$	2	1.90*	1.91*		
	3	2.02*	2.04*	2.07*	
	4	2.13*	2.13*	2.14*	2.14*
$[Cu(NH_3)_3(H_2O)_3]^+$	2	1.90*	1.90*		
	3	2.04*	2.04*	2.04*	
$[Cu(NH_3)_2(H_2O)_4]^+$	2	1.91*	1.91*		
	3	2.51	1.92*	1.92*	
$[Cu(NH_3)(H_2O)_5]^+$	2	1.90	1.90*		
	3	1.93	2.37	1.91*	
$[Cu(H_2O)_6]^+$	2	1.87	1.87		
	3	1.97	2.02	2.06	
	4	2.13	2.13	2.13	2.13

Values with and without * indicate Cu–N and Cu–O bonds, respectively.
Shortcut c.n. means coordination number.

Cu–N/Cu–O distances are also shortened by the presence of other molecules in the second shell. The reason can be seen in a fact that the electron density of N–H or O–H bonds in the ligand is decreased by the interactions of this positively charged hydrogen with a lone pair of electronegative atom from the second shell molecule. This induces a strengthening of the Cu–N/Cu–O dative bond in the complex. In the case of three-coordinated complexes, one of the bonds is usually longer than the remaining two. Interestingly, no five- or higher-coordinated complexes were found. Feller et al. [39] have studied the interactions of the Cu^+ cation with water using various ab initio approaches. Their Cu–O distances at the MP2/6-31+G(f)(RECP) level for all the (two- and three-coordinated) complexes match very well with our geometrical parameters. For the four-coordinated tetra-aqua system, we have obtained similar bond lengths but with the geometry in C_1 symmetry on the contrary to their structures in C_2 and S_4 point group of symmetry.

The optimized $[Cu(ligand)_K]^{2+}$ structures (where $K = 4$ or 6) are displayed in Fig. 2. The Cu(II) complexes prefer higher coordination, especially four- and in some cases also five-coordination. Actually, theoretical calculations performed by Schwenk and Rode [43] predict predominately six-coordinated structures of Cu(II) in liquid ammonia in case of HF QM/MM simulation, whereas the five- and six-coordinated complexes were obtained in a ratio of 2:1 in the B3LYP simulation case. This finding is in good agreement with our experience that the HF method exaggerates coordination number, e.g., in the Cu(I) case, the three-coordination is preferred over two-coordination as a global minimum in all the examined systems. The same authors have obtained the six-coordinated monoammine [1 + 5] and diammine [2 + 4] Cu^{2+} complexes in water [43]. There are also works devoted in four-coordinated copper structures, usually because of copper interaction with amino acids. For example, the extensive study of Katz et al. [2] has explored the tetraammine Cu(I)/Cu(II) structures. The pure ammine–copper(II) and aqua–copper(II) structures were subject of study performed by Berces et al. [45]. The authors have found that more than four-ligated complexes do not enhance the stabil-

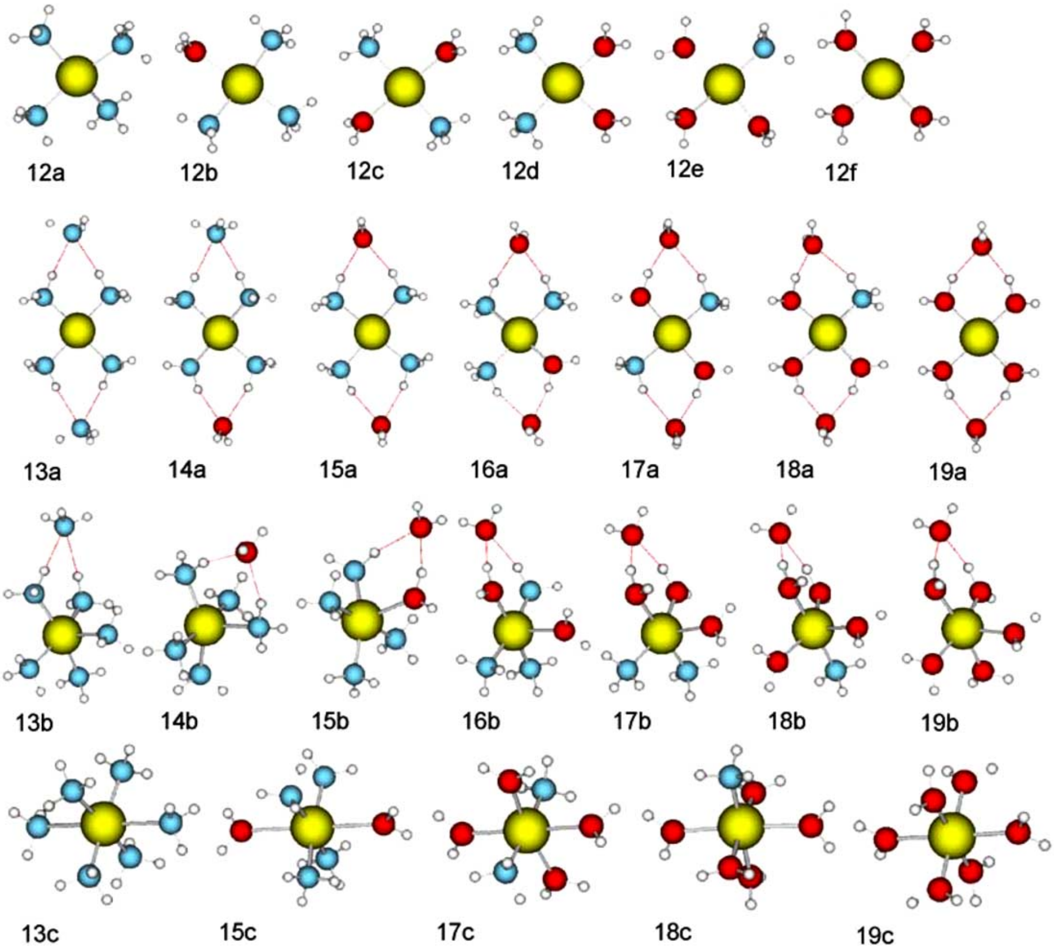

Fig. 2. (structures **12a**–**19c**) The optimized Cu(II) complexes. Systems **12a**–**f** represent four-coordinated $[Cu(NH_3)_m(H_2O)_n]^+$ structures ($m + n = 4$; $n = 0$ to 4). Systems **13**–**19** represent the $[Cu(NH_3)_m(H_2O)_n]^+$ structures ($m + n = 6$; $n = 0$ to 6). Letters a, b and c correspond to four-, five- and six-coordination.

ization energy of the molecule. However, there are also both experimental [50] and computational [47] studies which predict a coordination number six or even higher. Nevertheless, the calculations in the last mentioned paper were performed at the HF level, which reliability was discussed above.

Obtained copper–ligand distances are collected in Table 2. Shorter distances for Cu(II) complexes in comparison with the distances found in the Cu(I) systems indicate stronger Cu–L bonds. In analogy with the Cu^+ cation complexes, both Cu–N and Cu–O bond lengths shorten with number of aqua ligands. This fact is illustrated by the averaged coordination distances in Fig. 4. The only exception represents Cu–N bonds in the *trans*-$[Cu(NH_3)_2(H_2O)_2]^{2+}$ complex (structure **12d** in Fig. 2) due to a pronounced *trans*-effect. This conformer is not the lowest minimum of diammine-diaqua system. The *cis*-$[Cu(NH_3)_2(H_2O)_2]^{2+}$ complex (**12c**) possesses a lower energy and larger stabilization (see below).

The five-coordinated structures (**13**–**19b**) form the octahedral complexes, which are deformed by a missing axial vertex. Cu–L distances were found to be in very good agreement with other theoretical papers [2,42,43,45].

3.2. Energy

In order to analyze the optimized structures, the stabilization, coordination and sterically corrected energies were calculated at the DFT level of theory with the B3LYP functional and an extended triple-zeta basis set.

Table 3 contains the ΔE^{stab} stabilization energies for all the Cu(I) systems. Due to the fact that several molecules stay in second shell in the most of the explored structures (0–4a–b and 5–11a–c in Fig. 1), coordination energies ΔE^{coord} were calculated in order to estimate bonding energies per ligand.

From Table 3, it can be seen that two-coordinated complexes represent the global minima of the explored structures. This result is contradictive to the results obtained using the Hartree–Fock method that predict the three-coordinated Cu^+ systems as the global minima.

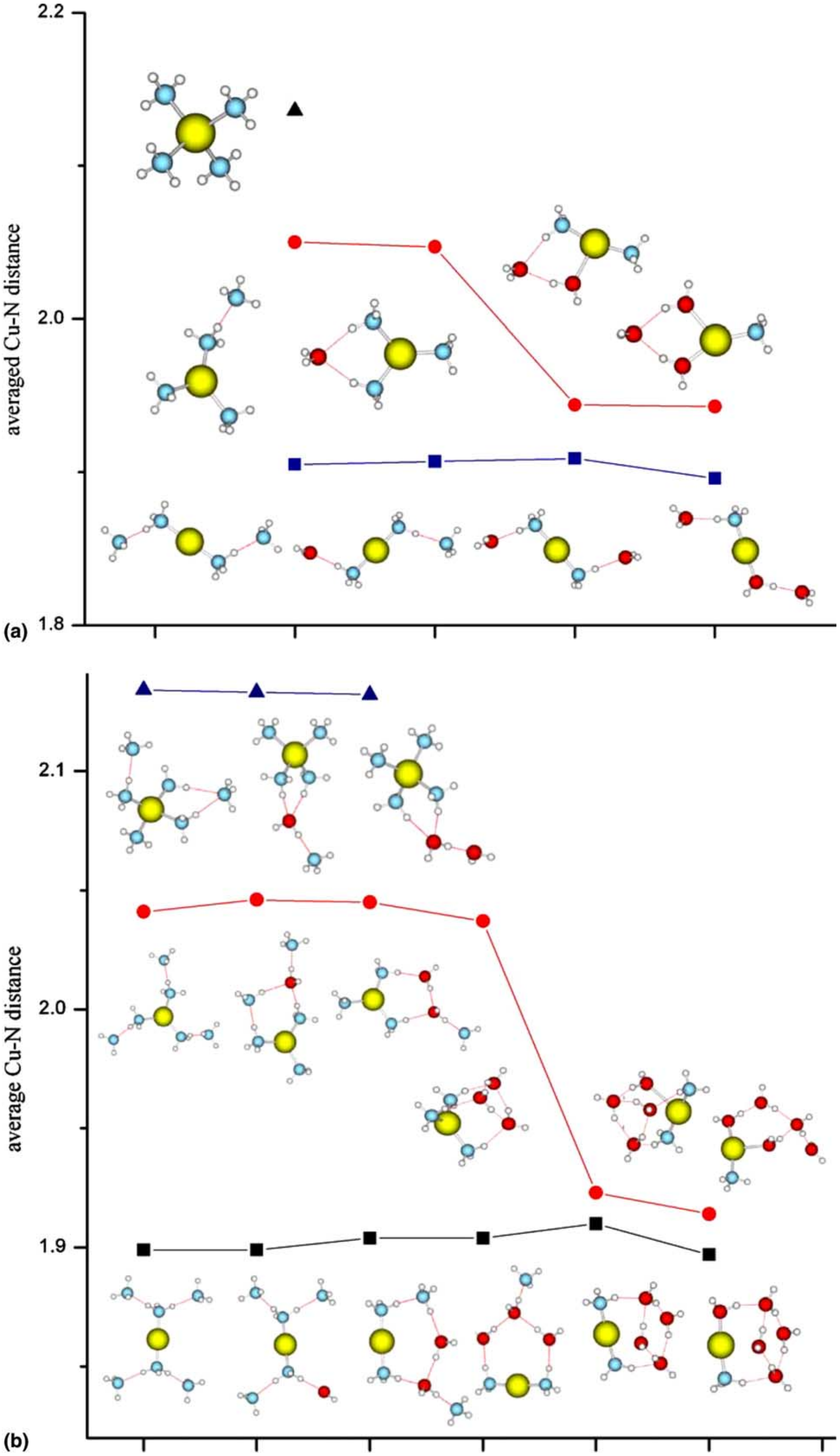

Fig. 3. (a) Dependence of the averaged Cu–N coordination bond lengths (in Å) for the $[Cu(NH_3)_m(H_2O)_n]^+$ structures ($m + n = 4$; $n = 0$ to 4) on increasing number of water molecules in system. ▲, for four-coordinated systems; ●, for three-coordinated systems and ■, for two-coordinated systems. (b) Dependence of the averaged Cu–N coordination bond lengths (in Å) for the $[Cu(NH_3)_m(H_2O)_n]^+$ structures ($m + n = 6$; $n = 0$ to 6) on increasing number of water molecules in system. ▲, for four-coordinated systems; ●, for three-coordinated systems and ■, for two-coordinated systems.

Table 2
Copper–ligand distances (in Å) for all presented Cu(II) complexes

System	c.n.	Cu–Lig1 (Å)	Cu–Lig2 (Å)	Cu–Lig3 (Å)	Cu–Lig4 (Å)	Cu–Lig5 (Å)	Cu–Lig6 (Å)
$[Cu(lig)_4]^{2+}$							
$[Cu(NH_3)_4]^{2+}$	4	2.05*	2.05*	2.05*	2.05*		
$[Cu(NH_3)_3(H_2O)]^{2+}$	4	2.01*	2.01*	2.04*	2.11		
cis-$[Cu(NH_3)_2(H_2O)_2]^{2+}$	4	2.00*	2.00*	2.02	2.02		
trans-$[Cu(NH_3)_2(H_2O)_2]^{2+}$	4	2.06*	2.06*	1.99	1.99		
$[Cu(NH_3)(H_2O)_3]^{2+}$	4	1.98*	1.98	1.99	2.01		
$[Cu(H_2O)_4]^{2+}$	4	1.96	1.96	1.96	1.96		
$[Cu(lig)_6]^{2+}$							
$[Cu(NH_3)_6]^{2+}$	4	2.04*	2.04*	2.04*	2.04*		
	5	2.07*	2.10*	2.10*	2.07*	2.28*	
	6	2.17*	2.17*	2.17*	2.17*	2.51*	2.51*
$[Cu(NH_3)_5(H_2O)]^{2+}$	4	2.04*	2.04*	2.04*	2.04*		
	5	2.08*	2.06*	2.07*	2.06*	2.30*	
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	4	2.05*	2.05*	2.05*	2.05*		
	5	2.08*	2.10*	2.08*	2.12*	2.24	
	6	2.06*	2.06*	2.06*	2.06*	2.60	2.58
$[Cu(NH_3)_3(H_2O)_3]^{2+}$	4	2.05*	2.05*	2.05*	2.05		
	5	2.04*	2.06*	2.03*	2.04	2.33	
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	4	2.01*	2.01*	1.98	1.98		
	5	2.04*	2.06*	2.03	2.04	2.33	
	6	1.99*	1.99*	2.18	2.18	2.35	2.33
$[Cu(NH_3)(H_2O)_5]^{2+}$	4	1.99*	1.98	1.97	1.96		
	5	1.99*	2.02	1.98	2.07	2.23	
	6	1.99*	2.10	2.10	2.00	2.30	2.29
$[Cu(H_2O)_6]^{2+}$	4	2.03	2.03	2.03	2.03		
	5	1.97	1.96	2.06	2.08	2.09	
	6	1.98	1.98	2.01	2.01	2.24	2.24

Values with and without * indicate Cu-N and Cu-O bonds, respectively.
Shortcut c.n. means coordination number.

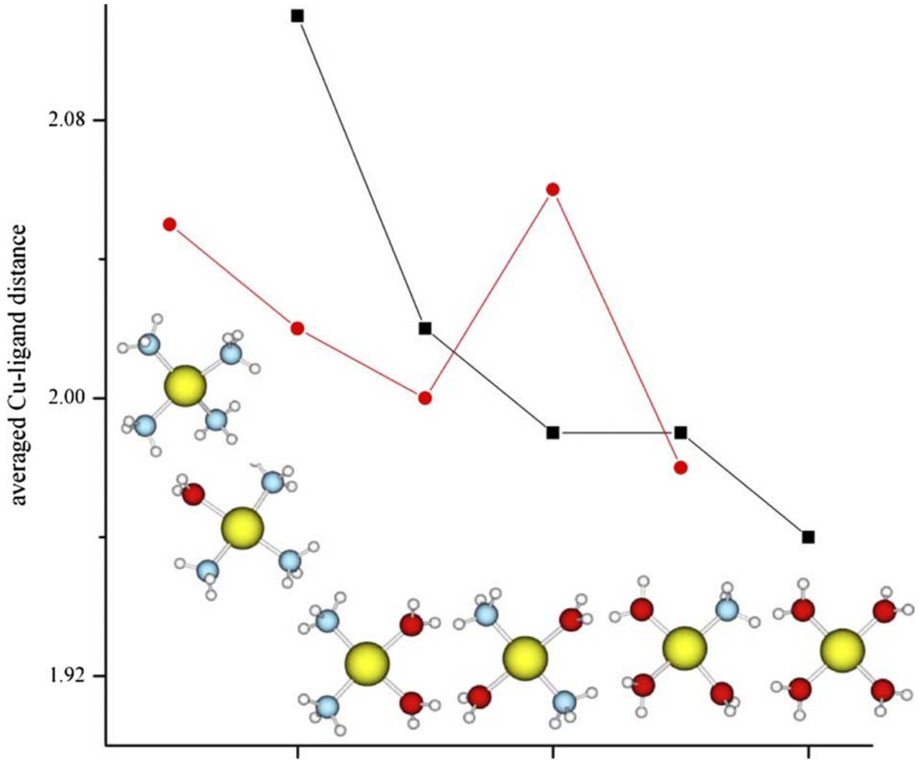

Fig. 4. The variation of averaged Cu(II)–N and Cu(II)–O distances (in Å) for the $[Cu(NH_3)_m(H_2O)_n]^{2+}$ ($m + n = 4$; $n = 0$ to 4) structures with number of water molecules. ●, for Cu–N bonds and ■, for Cu–O bonds.

Table 3
Stabilization ΔE^{stab} (total) and coordination ΔE^{coord} (related to a ligand bond) energies for all Cu(I) systems (in kcal/mol)

System	c.n.	E^{stab} (kcal/mol)	E^{coord} (kcal/mol)
$[Cu(lig)_4]^+$			
$[Cu(NH_3)_4]^+$	2	144.4	58.8
	3	140.5	43.3
	4	139.3	34.8
$[Cu(NH_3)_3(H_2O)]^+$	2	142.1	59.0
	3	140.6	43.2
$[Cu(NH_3)_2(H_2O)_2]^+$	2	139.8	59.2
	3	138.1	41.3
$[Cu(NH_3)(H_2O)_3]^+$	2	129.1	50.5
	3	126.9	36.3
$[Cu(H_2O)_4]^+$	2	117.6	41.8
	3	112.0	31.1
	4	106.7	26.7
$[Cu(lig)_6]^+$			
$[Cu(NH_3)_6]^+$	2	163.0	58.8
	3	158.5	43.1
	4	155.5	34.5
$[Cu(NH_3)_5(H_2O)]^+$	2	161.5	58.8
	3	161.1	43.2
	4	160.2	34.6
$[Cu(NH_3)_4(H_2O)_2]^+$	2	162.6	58.5
	3	162.6	42.9
	4	157.5	34.6
$[Cu(NH_3)_3(H_2O)_3]^+$	2	164.9	58.9
	3	159.3	43.0
$[Cu(NH_3)_2(H_2O)_4]^+$	2	162.7	59.0
	3	158.1	41.7
$[Cu(NH_3)(H_2O)_5]^+$	2	151.0	50.0
	3	149.6	36.5
$[Cu(H_2O)_6]^+$	4	142.2	41.1
	5	135.9	30.5
	6	132.9	25.1

Shortcut c.n. means coordination number.

Table 4
Selected terms from Morokuma energy decomposition analysis for some Cu(I) structures: electrostatic interaction E^{elec}, exchange energy E^{exch} and polarization energy E^{polar}

System	c.n.	E^{elec} (kcal/mol)	E^{exch} (kcal/mol)	E^{polar} (kcal/mol)
$[Cu(NH_3)_4]^+$	2	−226.1	196.7	−355.9
	4	−219.6	148.8	−89.7
$[Cu(NH_3)_3(H_2O)]^+$	2	−219.4	187.2	−351.1
$[Cu(NH_3)_2(H_2O)_2]^+$	2	−212.8	177.5	−346.2
$[Cu(NH_3)(H_2O)_3]^+$	2	−197.	167.6	−295.5
	3	−195.0	143.6	−197.8
$[Cu(H_2O)_4]^+$	2	−180.2	154.8	−244.2
	3	−169.3	118.9	−128.2
	4	−157.1	98.1	−84.2

Shortcut c.n. means coordination number.

In the complexes with higher coordination, the stabilization energy per bond rapidly decreases. The systems containing higher number of molecules quickly reach the saturation of the stabilization energy. Passing from 4 to 6 interacting molecules this energy is changed only due to the formation of H-bonds and Cu-remote molecule non-bonding interactions.

From water–ammonia arrangement in optimized systems, one can see that the ammine–Cu bond is stronger than aqua–Cu bond because ammine ligands are preferred in the first solvation shell. Actually, the Cu–N bonds are shorter in a presence of the directly ligated water molecules. As mentioned above, the stabilization energies correspond with stronger Cu–N than Cu–O interactions. This result is in agreement with the HSAB (hard-soft acid base) theory [71].

For some chosen Cu(I) complexes, Morokuma energy decomposition was computed (using RHF/6-31+G*) to acquire closer insight into the cation–ligand bonding. In Table 4, the basic contributions to the interaction are collected. On the contrary to relatively conserved electrostatic interaction, absolute values of polarization and exchange repulsion terms decrease with increasing of a coordination number. Nonetheless, the polarization energy decreases faster. Thus the lack of polarization energy causes the destabilization of the higher-coordinated complexes. The lower stabilization of Cu-complexes with the two aqua–ligands (two-coordinated system) can be explained by reduced polarization energy by ca. 50 kcal/mol per coordinated water molecule. For higher Cu-coordinations, the polarization contributions rapidly decrease so that relatively constant electrostatic term prevails. This is also demonstrated by the higher donation of the nitrogen electron density to copper atom (cf. discussion of partial charges bellow). From the polarization energies of pure tetraammine (−89.7 kcal/mol) and tetraaqua complexes (−84.2), it can be seen that it is practically constant for all tetra-coordinated species.

For the Cu(II) systems, stabilization (ΔE^{stab}) and sterically corrected stabilization (ΔE^{stex}) energies are presented in Table 5. The dependence of ΔE^{stab} in the $[Cu(NH_3)_m(H_2O)_n]^{2+}$ structures (**13a**–**19c**) is also shown in Fig. 5 for better insight. In analogy to Cu(I) complexes, Cu–N bonds were found stronger than Cu–O one. Therefore stabilization of the whole system depends basically on the number of ammine ligands in the first coordination shell. But unlike Cu^+ structures, higher coordination is preferred, namely four-coordination.

In case of the $[Cu(NH_3)_6]^{2+}$ systems (**13a**–**c**), five-coordinated Cu(II) cation is practically degenerated to four-coordinated complex. The stabilization energy of the five-coordinated complex is about 0.4 kcal/mol smaller. It is within the error of the energy determination. When the corrections on sterical repulsion are taken into account, the pure Cu–N bonding energy is larger in the five-coordinated systems (by 7 kcal/mol). Also six-coordinated system has its ΔE^{stex} larger than four-coordinated one.

Similar situation occurs for the $[Cu(NH_3)_5H_2O]^{2+}$ system, where one water molecule remains in outer shell, leaving the directly bonded $[Cu(NH_3)_n]^{2+}$ complex prac-

Table 5
Stabilization ΔE^{stab} and sterically corrected stabilization ΔE^{stex} energies for all Cu(II) systems (in kcal/mol)

System	c.n.	E^{stab} (kcal/mol)	E^{stex} (kcal/mol)
[Cu(lig)$_4$]$^{2+}$			
$[Cu(NH_3)_4]^{2+}$	4	366.8	391.8
$[Cu(NH_3)_3(H_2O)]^{2+}$	4	353.6	376.6
cis-$[Cu(NH_3)_2(H_2O)_2]^{2+}$	4	340.2	359.5
trans-$[Cu(NH_3)_2(H_2O)_2]^{2+}$	4	339.7	359.9
$[Cu(NH_3)(H_2O)_3]^{2+}$	4	323.5	340.0
$[Cu(H_2O)_4]^{2+}$	4	306.9	321.1
[Cu(lig)$_6$]$^{2+}$			
$[Cu(NH_3)_6]^{2+}$	4	407.5	437.7
	5	407.1	444.6
	6	399.9	443.7
$[Cu(NH_3)_5(H_2O)]^{2+}$	4	406.8	437.8
	5	404.6	441.6
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	4	406.2	438.0
	5	402.7	435.1
	6	398.4	435.8
$[Cu(NH_3)_3(H_2O)_3]^{2+}$	4	398.4	425.2
	5	395.5	425.1
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	4	389.4	411.1
	5	385.2	409.6
	6	379.7	411.6
$[Cu(NH_3)(H_2O)_5]^{2+}$	4	376.9	393.6
	5	372.9	393.4
	6	366.3	394.5
$[Cu(H_2O)_6]^{2+}$	4	363.4	376.4
	5	358.6	377.1
	6	338.0	362.2

Shortcut c.n. means coordination number.

tically unchanged in comparison with the hexaammine system ($n = 4$ or 5). In remaining mixed ammonia–water compounds, the differences in the sterical repulsion correction between ligands are not so large going from four- to six-coordinated complexes to be able to change the order of the ΔE^{stex} values in comparison with ΔE^{stab} (like it was seen in the $[Cu(NH_3)_6]^{2+}$ or $[Cu(NH_3)_5(H_2O)]^{2+}$ cases). Thus, similar order of ΔE^{stab} and ΔE^{stex} values for the coordination number varying from 4 to 6 is visible from Table 5 preferring the coordination number of 4 (or 5).

In case of the hexaaqua complexes (**19a**–**c**), the six-coordination arrangement displays the largest energy $\Delta E^{stab}(4) - \Delta E^{stab}(6)$ difference (25.4 kcal/mol) among all ammonia–water systems.

Similar results were published by Berces et al. [45] for the pure ammine–Cu(II) and aqua–Cu(II) complexes. A good agreement in differences of stabilization energies between four-, five- and six-coordinated species was obtained. They found an energy preference for four- over five-coordination by about 4 and 1 kcal/mol for the $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_6]^{2+}$ systems, respectively. In the present study, the corresponding differences are 5 and 0.5 kcal/mol. They also predict a lower stabilization of six-coordination (compared to four-coordination) by about 14 and 25 kcal/mol for the $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_6]^{2+}$ systems, respectively. This matches with our results where these differences were determined to be 25 and 8 kcal/mol.

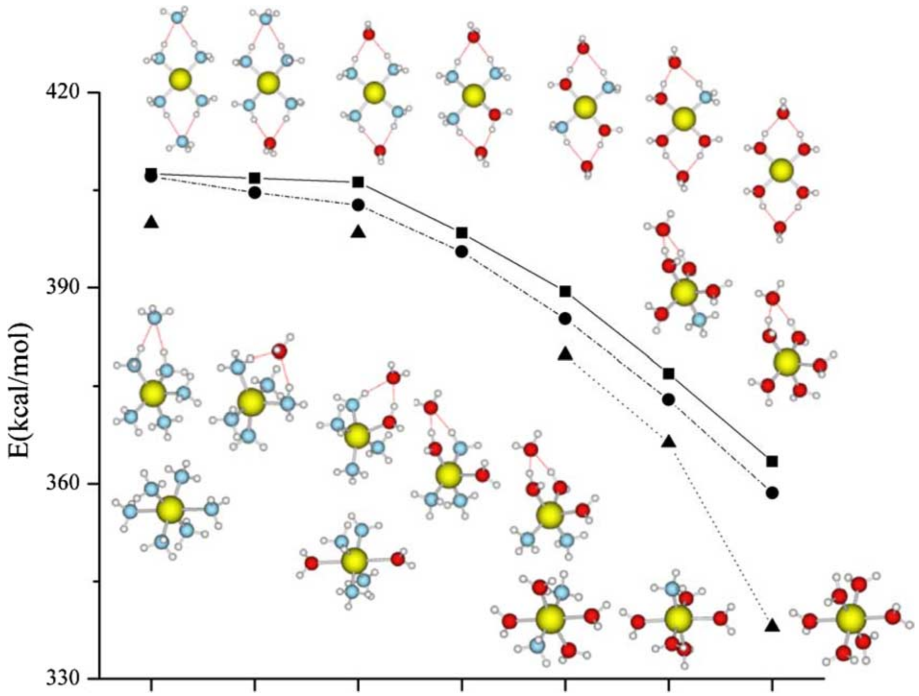

Fig. 5. The trend of stabilization energies (in kcal/mol) for the $[Cu(NH_3)_m(H_2O)_n]^{2+}$ complexes ($m + n = 6$; $n = 0$ to 6) in dependence on the number of water molecules. ▲, for six-coordinated systems; ●, for six-coordinated systems and ■, for four-coordinated systems.

As to four-molecular systems, it is worth to point to a very small difference between the *cis*-[Cu(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ and *trans*-conformer that is less than 1 kcal/mol. Similar preference was also published in paper [43].

3.3. Charge analyses

In order to get deeper insight into the dependences of the energy and geometry parameters, the partial charges based on natural population analysis (NPA) were determined. In addition, occupations of some important Cu atomic orbitals were explored, too. Both quantities are presented in Tables 6 and 7 for the Cu(I) and Cu(II) systems, respectively.

For the donation of the electron lone pairs from ligands, the vacant Cu orbitals play the fundamental role, especially 4s AO. Hence, its occupation was used for quantification of the strength of dative bonds in the case of Cu(I) complexes. In the two-coordinated Cu$^+$ systems, the donation is remarkably higher (0.56e) than for the three- (0.34e) and four-coordination (0.24e in case of the [Cu(NH$_3$)$_4$]$^+$ system). Similar trend is also evident in the [Cu(NH$_3$)$_6$]$^+$ complex and generally in all the examined Cu(I) systems. Higher occupation of 4s orbital correlates with stronger coordination-covalent character of such bonds and matches with the pronounced polarization energies in two-coordinated complexes as mentioned above when the Morokuma's energy decomposition was discussed. Decreased occupation of 4s Cu AO with increasing number of aqua ligands is in correspondence with the lower water polarizability and lower donation ability since the water lone pairs are not usually oriented in Cu–O bond direction as it was stressed in our previous paper [64]. Partial charge on the Cu$^+$ cation varies from 0.63e (for the two-coordinated hexaammine complexes) to 0.80e (for the two-coordinated tetra-aqua complexes). The influence of additional molecules in outer solvation shell on the occupation of copper 4s AO and on the partial charge of Cu atom is only marginal.

Investigation of the divalent copper structures is a little more complicated since the donation also partially increases the occupation of SOMO [72]. Therefore, only the net charge distribution represents the unique criterion for the donation extent. From data presented in Table 7, one can see that the smallest positive Cu partial charge appears for the four-coordinated complexes. This reflects the largest electron

Table 6
Occupations of Cu 4s AO and the partial charges on copper for all presented Cu(I) systems (in e)

System	c.n.	4s	δ (Cu)
[Cu(lig)$_4$]$^+$			
[Cu(NH$_3$)$_4$]$^+$	2	0.56	0.65
	3	0.34	0.76
	4	0.24	0.80
[Cu(NH$_3$)$_3$(H$_2$O)]$^+$	2	0.55	0.66
	3	0.34	0.76
[Cu(NH$_3$)$_2$(H$_2$O)$_2$]$^+$	2	0.55	0.66
	3	0.44	0.73
[Cu(NH$_3$)(H$_2$O)$_3$]$^+$	2	0.48	0.73
	3	0.33	0.81
[Cu(H$_2$O)$_4$]$^+$	2	0.41	0.80
	3	0.24	0.87
	4	0.19	0.88
[Cu(lig)$_6$]$^+$			
[Cu(NH$_3$)$_6$]$^+$	2	0.59	0.63
	3	0.34	0.75
	4	0.26	0.80
[Cu(NH$_3$)$_5$(H$_2$O)]$^+$	2	0.58	0.63
	3	0.35	0.75
	4	0.25	0.80
[Cu(NH$_3$)$_4$(H$_2$O)$_2$]$^+$	2	0.55	0.66
	3	0.34	0.76
	4	0.25	0.80
[Cu(NH$_3$)$_3$(H$_2$O)$_3$]$^+$	2	0.55	0.66
	3	0.32	0.77
[Cu(NH$_3$)$_2$(H$_2$O)$_4$]$^+$	2	0.53	0.67
	3	0.48	0.71
[Cu(NH$_3$)(H$_2$O)$_5$]$^+$	2	0.47	0.73
	3	0.41	0.77
[Cu(H$_2$O)$_6$]$^+$	2	0.45	0.77
	3	0.23	0.87
	4	0.14	0.89

Shortcut c.n. means coordination number.

Table 7
Occupations of Cu 4s and 3d$_{x2\text{-}y2}$ AOs and the partial charges on copper for all presented Cu(II) systems (in e)

System	c.n.	4s	3d($x^2 - y^2$)	δ (Cu)
[Cu(lig)$_4$]$^{2+}$				
[Cu(NH$_3$)$_4$]$^{2+}$	4	0.36	1.39	1.30
[Cu(NH$_3$)$_3$(H$_2$O)]$^{2+}$	4	0.33	1.40	1.36
cis-[Cu(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$	4	0.31	1.31	1.40
trans-[Cu(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$	4	0.32	1.29	1.41
[Cu(NH$_3$)(H$_2$O)$_3$]$^{2+}$	4	0.28	1.38	1.48
[Cu(H$_2$O)$_4$]$^{2+}$	4	0.24	1.24	1.56
[Cu(lig)$_6$]$^{2+}$				
[Cu(NH$_3$)$_6$]$^{2+}$	4	0.37	1.38	1.27
	5	0.34	1.32	1.33
	6	0.34	1.30	1.35
[Cu(NH$_3$)$_5$(H$_2$O)]$^{2+}$	4	0.37	1.38	1.27
	5	0.34	1.34	1.34
[Cu(NH$_3$)$_4$(H$_2$O)$_2$]$^{2+}$	4	0.37	1.38	1.27
	5	0.33	1.34	1.34
	6	0.33	1.36	1.34
[Cu(NH$_3$)$_3$(H$_2$O)$_3$]$^{2+}$	4	0.34	1.36	1.33
	5	0.32	1.31	1.38
[Cu(NH$_3$)$_2$(H$_2$O)$_4$]$^{2+}$	4	0.31	1.29	1.41
	5	0.30	1.30	1.42
	6	0.28	1.36	1.46
[Cu(NH$_3$)(H$_2$O)$_5$]$^{2+}$	4	0.29	1.27	1.46
	5	0.26	1.32	1.50
	6	0.25	1.29	1.52
[Cu(H$_2$O)$_6$]$^{2+}$	4	0.26	1.24	1.56
	5	0.24	1.22	1.56
	6	0.24	1.43	1.64

Shortcut c.n. means coordination number.

donation and the largest polarization energy contribution in analogy with the Cu(I) systems. The interesting situation was found for the Cu(II) systems with 6 water molecules (structures **19a–c**). Here, nearly the same partial charges for four- and five-coordination can be observed. Since the water polarizability and donation ability is low as already mentioned above, the electrostatic part prevails and the changes in polarization are minimal. Generally, the deviations from the hypothetical 2+ charge of the Cu cation are quite large. Partial charges vary from 1.27e for tetraammine coordinated complexes (**13a**) to value 1.64e for the complexes with six coordinated water molecules (**19c**). The results can also be compared with work of Katz et al. [2] for tetraammine systems. They obtained at the MP2/LANL2DZ(d) level partial charges of 0.87e and 1.65e for their Cu(I) and Cu(II) complexes, respectively. Corresponding values from Tables 6 and 7 are 0.80 and 1.30e. This discrepancy in the Cu(II) case can be explained by the different geometry, since their Cu(II) complex have not the square planar symmetry.

4. Conclusion

In the present study, the various-coordinated [Cu-$(NH_3)_m(H_2O)_n]^{2+/+}$ complexes were examined where n ranges from 0 to 4 or and $m + n = 4$ or 6. After the B3PW91/6-31+G(d) optimizations, single-point calculations of the stabilization energies including the BSSE and deformation corrections were performed at the B3LYP/6-311++G(2df,2pd) level of theory. It was found that the most stable Cu(I) and Cu(II) complexes are the two-coordinated and four-coordinated structures, respectively. Actually, some five-coordinated complexes of Cu^{2+} are fairly stable, too. The most preferable coordination numbers were discussed and compared with other works [3,42,43,45,46,50,57].

The most stable structures exhibit the shortest Cu–N (1.9/2.05 Å for Cu(I)/Cu(II) species) and Cu–O bonds (1.87/1.96 Å). Obtained distances of all the explored compounds are also in very good agreement with the results of other studies [2,42,43,45,57].

In addition, the donation effect was investigated in terms of the copper partial charge and occupation numbers of Cu 4s and 3d AOs using the NPA method. The analysis explains the strongest copper coordination-covalent interactions with 2 ligands in monovalent, and 4 ligands in divalent systems by the most pronounced electron density redistribution. The both energetic and wave function analyses also confirm copper–ammine bonding to be preferred over copper-aqua one. Thus, mixed water/ammonia complexes always prefer to form structures with the NH_3 molecules in the first hydration shell. Moreover, the Morokuma energy decomposition analysis enlightens the role of Coulomb, exchange repulsion and polarization terms at the Hartree-Fock level of theory.

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