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Theoretical model of copper Cu(I)/Cu(II) hydration. DFT and ab initio quantum chemical study

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Abstract

Hydration study of both Cu^+ and Cu^{2+} cations in variable water environment was performed using the DFT method. After optimization using B3PW91 functional, stabilization energies with and without ligand repulsion were calculated using B3LYP functional. It was found that optimal Cu^+ coordination involves two directly bonded solvent molecules while Cu^{2+} cation prefers 4 (or 5) coordinated waters in the first solvation shell. Higher coordination corresponds to lower stabilization energies. Morokuma's energy decomposition (for Cu^+ complexes only) was used to elucidate bonding characteristics in detail. NBO partial charges and MO's analyses support the explanation for these energy results.
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1. Introduction

There can be found large abundance of theoretical papers in biodisciplines, which concern to interaction of copper cations with DNA/RNA bases [1–4]. Some experimental structures are available for comparison [5–9]. Interactions with amino acids are computed in works [10–16]. Also for these calculations, one can find many experimental evidences, e.g. in works [17,18]. Great attention is directed to solve structures and clarify properties of so-called blue proteins. Basic role of the copper Cu(I)/Cu(II) redox possibility can be demonstrated on their models. Blue copper proteins are a group of electron transfer proteins characterized by several unusual properties—bright blue color, narrow hyperfine splitting in the electronic spin resonance spectra and high reduction potentials. The Cu ion is bound to the protein in an approximate trigonal plane formed by a cystine (Cys) thiolate group and two histidine (His) nitrogen atoms. In most of these blue copper proteins, the coordination sphere is completed with one or two S-ligands, typically a methionine (Met) thioether group, but

sometimes also of a carbonyl oxygen atom from the side chain of glutamine. Such geometry is similar to what can be expected for Cu(I) complexes. Copper coordination geometries of reduced blue copper proteins are very close to those of the oxidized proteins [19–26]. Some interesting experimental works on charge transfer on blue peptides were recently published [27,28], which enable comparison with theoretical studies.

Copper is a part of some oxidation enzymes—indophenoloxidases, and is also present in fourth cycle of respiration chain in the so-called terminal oxidation operating as redox center of metalloprotein. It is included in many other biomolecules, for example: cytochrom *c* oxidase, superoxidase dismutase, tyrosinase [29], and many other. All of them require copper in the active sites in order to be biochemically active [30].

Water is the most usual environment for solvation. Consequently, contribution of this work is a closer insight in mechanisms of copper Cu(I)/Cu(II) cations interactions with water molecules. There could be seen some basic differences between the coordination of both copper cations which are important in many vivo processes, as mentioned above. Importance of this very simple model is reflected in number of papers studying copper hydration using either

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static [31,32] or dynamic [33,34] approach or both [35–38]. Also Cu(I) hydration was thoroughly explored by Feller et al. [39]. Experimental work in gas phase confirms high stability of some low-coordinated Cu(II) complexes [40].

Some effort was also devoted to design parameters for empirical force field [41–43] to enable faster classical MD approach to such problems.

In work of Luna, difficulties at G2 level of Gaussian theory were noticed dealing with copper complexes [44] on the contrary to DFT calculations and similar problems were also noticed for calculations with QCISD method [45].

The aim of the present study is to describe stable-coordinated structures of Cu(I) and Cu(II) interacting with one to six water molecules. For the examination of these systems, geometric, energetic and population analyses have been done.

Next objectives to study are stability and energetic relations between structures with various coordination numbers, deformation of molecules interacting with Cu^+ and Cu^{2+} atoms, verification of Jahn–Teller first and second order effect on the copper complexes and a comparison of our results with calculations presented in works of other authors [33,46,47].

2. Computational details

All the $[Cu(H_2O)_n]^+$ structures (where $n = 1$–6) are closed shell systems with singlet electron configuration. Geometry optimization was performed at DFT level with B3PW91 functional, which compared to B3LYP functional gives slightly better structure results and vibrational properties [48–51]. Although geometries obtained by B3LYP are not qualitatively different. The standard $6\text{-}31 + G(d)$ basis set was chosen with added polarization and diffuse functions due to the fact that enhanced variation of copper wide 4s AO provides the satisfaction of the donation effects. Hence, it strongly affects stabilization of some Cu(I) complexes. The Cu atom was described by averaged relativistic effective pseudopotentials (AREP) [52], extended by a set of diffuse ($\alpha_s = 0.025$, $\alpha_p = 0.35$, and $\alpha_d = 0.07$) and polarization ($\alpha_f = 3.75$) functions. Several structures, which differ usually by rotation of water molecules around the Cu–O axe or by different H-bonding pattern, were found in a few kilocalorie per mole range. This made the optimization and the following single-point analyses slightly more demanding. In the discussion part, only global minima are mentioned. Some local minima were presented in study [39]. Energy characteristics and charge distribution analysis were performed on the optimized structures using B3LYP functional and $6\text{-}311 + +G(2df,2pd)$ basis set on oxygen and hydrogen atoms. Set of AOs on the Cu atom was enlarged 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. The exponents were optimized using CCSD method on

the ground state electronic configuration $^2X(Cu)$. The stabilization energies with their appropriate counterpoise corrections [53] (including BSSE and deformation corrections) were calculated according to formula:

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

where $E_{monomer}$ denotes the energy of the given monomer including the AOs of ghost atoms. Besides the ΔE^{Stab} energies, sterically corrected stabilization ΔE^{Stex} was determined, too. In this case, all the ligands were considered as one 'monomer' and central Cu cation as another. The third characteristics—coordination energy ΔE^{coord} was considered in the case of Cu(I) interactions where some water molecules stay in second hydration shell. The coordination energy is evaluated like ΔE^{Stab} when only directly bonded water ligands are considered using the geometry optimized for the whole complex.

Since the Cu^{2+} ion is an open shell system with 3d [9] valence electron configuration, the Cu(II) complexes were considered as doublets. Therefore, determination of the correct wave function had to be done with care. The correct wave function was constructed in reduced basis set with Restricted Open Shell Hartree-Fock (ROHF) procedure first. When correct occupation was obtained, bigger basis $6\text{-}31 + G^*$ was used and UHF geometry optimization performed. Finally, DFT re-optimization was done. In analogy to Cu(I) complexes, several local minima, which are not presented here (some of them can be found, e.g. in Ref. [35]), are close in energy. Determination of energy characteristics and charge distribution analyses were solved using B3LYP functional in $6\text{-}311 + +G(2df,2pd)$ basis in analogy to Cu(I) systems. For Natural Population Analysis (NPA) [54], 1g function had to be removed because used program GAUSSIAN 98 [55] did not support NPA with g functions. These methodology was applied to coordinated structures including divalent copper in water ligand fields $[Cu(H_2O)_n]^{2+}$ ($n = 1,...,6$). Morokuma decomposition analysis was performed using GAMESS-US program [56] for hydrated Cu(I) systems.

Visualization of geometries, MOs, and vibrational modes was done with programs MOLDEN 4.0 [57] and MOLEKEL 4.3 [58,59].

3. Results and discussion

The goal of the optimization process for Cu(I) complexes was to find stable-coordinated structures. A problem dwells in very similar values of copper-ligand bond energy at one side and H-bonding of water molecules in second solvation shell on the other side. Therefore, it was difficult to find more than 3-coordinated structures and no stable 5- and 6-coordinated Cu(I) structures were found.

Table 1
The Cu–O distances and average Cu–O distances (in Å)

System	c.n.	Cu–O1	Cu–O2	Cu–O3	Cu–O4	Cu–O5	Cu–O6	Average Cu–O
$[Cu(H_2O)]^+$	1	1.929						1.929
$[Cu(H_2O)_2]^+$	2	1.899	1.899					1.899
$[Cu(H_2O)_3]^+$	2	1.903	1.873					1.888
	3	1.944	1.959	2.249				2.051
$[Cu(H_2O)_4]^+$	2	1.878	1.878					1.878
	3	1.970	1.976	2.143				2.030
	4	1.998	2.085	2.207	2.257			2.137
$[Cu(H_2O)_5]^+$	2	1.883	1.863					1.873
	3	1.932	1.974	2.180				2.029
$[Cu(H_2O)_6]^+$	2	1.866	1.866					1.866
	3	1.969	2.019	2.058				2.015
	4	2.126	2.126	2.126	2.126			2.126
$[Cu(H_2O)]^{2+}$	1	1.864						1.864
$[Cu(H_2O)_2]^{2+}$	2	1.852	1.852					1.852
$[Cu(H_2O)_3]^{2+}$	3	1.901	1.901	1.911				1.904
$[Cu(H_2O)_4]^{2+}$	4	1.960	1.960	1.959	1.963			1.961
$[Cu(H_2O)_5]^{2+}$	4	1.939	1.941	1.972	1.977			1.957
	5	2.170	2.013	1.974	2.013	1.974		2.029
$[Cu(H_2O)_6]^{2+}$	4	1.956	1.956	1.956	1.956			1.956
	5	1.974	1.975	1.998	2.008	2.212		2.033
	6	2.026	2.026	2.003	2.003	2.281	2.281	2.103

c.n., the coordination number.

3.1. Structures of Cu(I)/Cu(II) hydrates

Described methodology was applied on systems of monovalent copper cation (Cu^+) and variable number of water molecules. It was found for $[Cu(H_2O)_n]^+$ structures, that only 1, 2, 3 and 4-coordinated structures form stable minima. The Cu–O distances for ligated waters are compiled in the first part of Table 1.

Short distances for 2-coordinated Cu(I), remarkable from the Table 1, are an interesting feature of these systems. They are even shorter than in case of $[Cu(H_2O)]^+$ where only one Cu–O bond exists (1.929 Å). Possible explanation of this fact insists in surprisingly small donation of single water. This is supported by the facts that partial charge on Cu cation in single-water system is much higher ($+0.96$— practically unchanged by interaction with water) than in the rest of investigated complexes, and polarization and charge transfer terms are very small in comparison with other systems, when Morokoma's energy decomposition is performed (cf. below). From all the explored systems, where n waters ($n>1$) interact with Cu(I), the 2-coordinated complexes represent the most stable ones. Distinct shortening of Cu–O bond with higher numbers of water molecules in second shell is visible from Table 1. The shortest average distance is 1.866 Å in 2-coordinated $[Cu(H_2O)_6]^+$ complex.[1] The 3-coordinated complexes

always have smaller stabilization energy and their structures exhibit marked deformation: one of the bonds is usually longer than the other two and large deviations from 120 degrees occur for O–Cu–O valence angles. The largest deformation occurs for 'isolated' $[Cu(H_2O)_3]^+$ without any water in second shell. Outer waters stabilize the dative coordination interactions in the same way like in 2-coordinated complexes. Analogous effect is also noticeable in 4-coorditated complexes where two additional outer water molecules make the four coordination bonds equivalent, on the contrary to $[Cu(H_2O)_4]^+$ complex. However, this quasi-equivalence is connected with substantial change of geometry. While $[Cu(H_2O)_4]^+$ system has a shape of deformed trigonal pyramide, 4-coordinated $[Cu(H_2O)_6]^+$ system is a flattered tetraeder. Interestingly, in the case of five water molecules no stable 4-coordinated structure was found, probably due to highly asymmetrical destabilization of single outer water.

In case of $[Cu(H_2O)_6]^{2+}$ structure, some other results are available, e.g. in Ref. [33] Cu–O distances are 2.07 Å for equatorial and 2.24 Å for axial bonds, which is in very good accord with our data in Table 1. Also the Ziegler group [35] published extensive work with structures of Cu(II) hydrates, which match with our data closely, e.g. $d(Cu–O) = 1.965$ and 1.923 Å for 3-coordinated triaqua complex or $d = 1.983$, 1.997, 1.997, 2.011 in $[Cu(H_2O)_4]^{2+}$ complex.

As to H-bond lengths, 3 different types can be found. First, in 2-coordinated complexes, 1–4 molecules were attached to one of the four hydrogens of coordinated ligands. These H-bonds are the shortest (<1.70 Å). In 3- or 4-coordinated complexes, usually 6-member rings appear

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[1] HF results differ in this point preferring usually 3-coordinated complexes as the global minima. This is due to larger accent on electrostatic and polarization interactions in uncorrelated HF method. Also, 6-coordinated complex was found as a stable local minimum at the HF level.
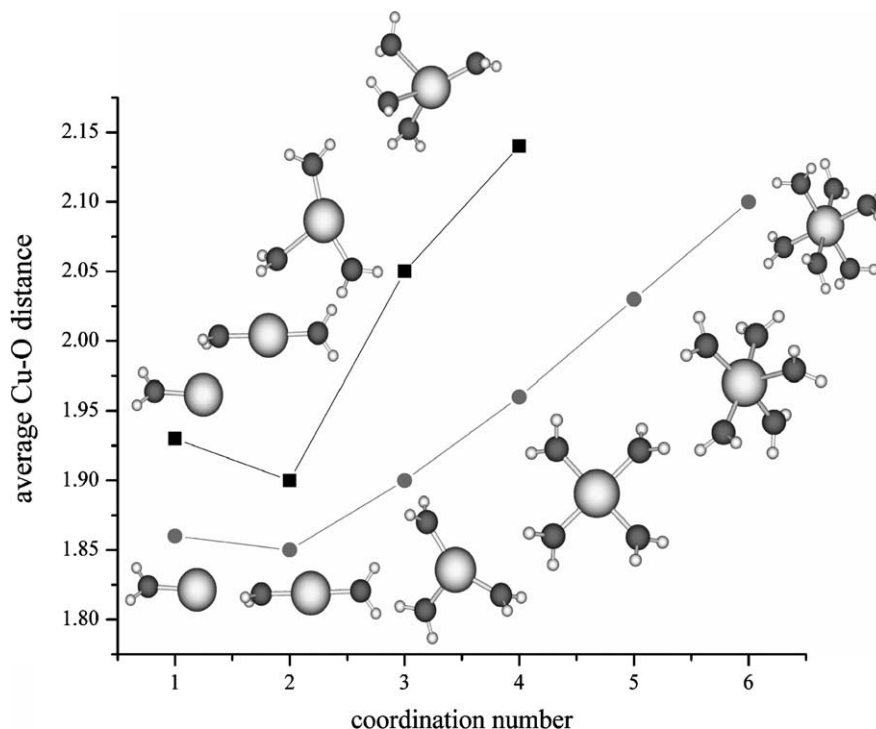
Fig. 1. The average Cu–O distances of the Cu(I)/Cu(II) aqua-systems in Å units.

with two H-bonds, which have protons from ligated waters oriented towards oxygen in outer solvent molecule. Such H-bonds exhibit usually distances in the range 1.70–1.85 Å. At last, H-bonds between waters in second solvation shells of higher-member rings have distances slightly above 1.85 Å. In such rings, first and third types of H-bonds are mixed. From many papers, which deal with pure water clusters, e.g. Refs. [60–64] it can be seen that the usual H-bond length is about 1.81–1.88. This is in good accord with our findings since water molecules from the first (and partially also from the second) solvation shells are polarized by Cu^+ cation, which causes slightly shorter H-bonds.

In the case of Cu(II) complexes, different relations were found. The higher coordination is substantially more stable. Global minima are usually 4-coordinated complexes but 5-coordinated complexes are in very close proximity (within 2–5 kcal/mol, cf. below). This is in very good accord with recent experimental discovery: 5-coordinated water complexes were measured with extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) [65]. In this work, theoretical approach (CPMD) was also used and a very good accordance for the pair correlation functions $g_{CuO}(r)$ and XANES spectra was obtained.
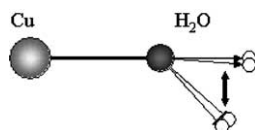
Shorter distances basically indicate stronger Cu–O bonds. Thus an estimation of the complex stability can be obtained from Table 1 or/and Fig. 1. In analogy with $[Cu(H_2O)]^+$, the Cu–O bond distance for monoaqua complex is slightly longer than for diaqua-structure. The explanation is similar— smaller donation of water lone pair (cf. below). The difference is much smaller here, however. A minimum can be observed in Fig. 1 where Cu–O bond length dependences on water coordination number are drawn.

Interesting situation concerns the deviation angle of the Cu–O bond from the water-molecule plane (cf. Scheme 1). While in $[Cu(H_2O)]^+$ this bond lies nearly in the plain (8°), approximately 26° deviation occurs in Cu(II) case. The situation is changed for diaqua-complexes—19° in Cu(I) complex vs. 14° in Cu(II) one. In case of 3- and 4-coordinated Cu(I) structures,
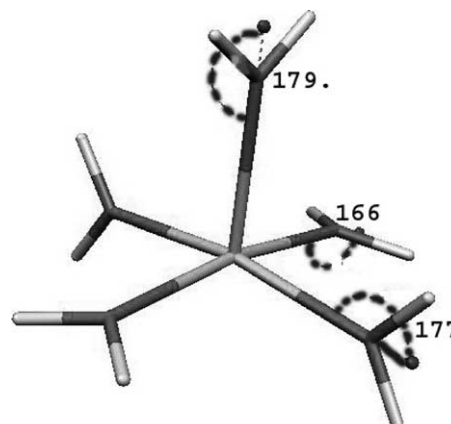

Scheme 1.

Fig. 2. The angle between the Cu–O line and H–O–H plane.

these angles are above $20°$, while analogous Cu(II) complexes have Cu–O bond practically in the water plain (deviation $<6°$). The only exception is a deformed octahedral pentaaqua-complex (cf. Fig. 2). Nonplanarity appears in order to minimize repulsion among Cu and hydrogens. In Cu^+ complexes, a weaker repulsion between partial charges on hydrogens and copper cation cannot push out Cu–O from 'optimal' position, corresponding to dative character, which follows a higher electron density of one of the lone pairs in sp^3 configuration on the oxygen. Since $[Cu(H_2O)]^+$ exhibits very small donation, the angle is governd by the electrostatic repulsion only.

3.2. Hydration energies

3.2.1. Cu(I) complexes

After geometry optimization using the B3PW91 functional, stabilization energies (with and without sterical repulsion) were calculated. In Table 2, stabilization energies ΔE^{Stab} and sterically corrected stabilizations ΔE^{Stex}, are collected. Since several water molecules stay in second hydration shell when Cu^+ cation interacts with higher number of water molecules, coordination energies were calculated in such cases, too.

From the first two rows, it can be seen that longer Cu–O bond distance in monoaqua than in diaqua Cu(I) complexes reflects in the stabilization energies. However, stabilization of these two complexes per bond is nearly the same (cf. Fig. 3a). In complexes with higher coordination, the stabilization energy per Cu–O bond rapidly decreases. While optimized 3-coordinated complexes represent local minima on potential energy surface for systems with any larger number of water ($n \geq 3$), 4-coordinated complex was found as a stable local minimum only in 4 and 6 watered systems. On the contrary, Hartree-Fock optimizations predict 3-coordinated Cu^+ complexes as global minima, as mentioned above.

Higher number of water molecules exhibits rapid saturation in stabilization energy. Passing from 5 to 6 interacting waters, the total stabilization energy is increased only by 12 kcal/mol. This is just an energy of one additional H-bond in linear 2-coordinated structure (global minimum). Values of coordination energies demonstrate small influence of water molecules from the second shell on the dative bonds, i.e. coordination energies ΔE^{coord} vary less than 1 kcal/mol with number of outer waters. The stabilization energy increase for the first water in second hydration shell is about 18 kcal/mol (difference between ΔE^{Stab} and ΔE^{coord}) and it goes to 15 kcal/mol per one H-bond in the 2-coordinated system with six interacting solvent molecules, cf. Fig. 3a. This cannot be regarded as a pure H-bond strength since interaction with remote Cu cation is also involved. Nevertheless, it can be seen that the dominant part is of H-bonding origin (between polarized (ligated) water…water (outer)). Complete occupation of the second shell will probably decrease this energy to ca. 10–12 kcal/mol that is already close to situation in pure water clusters (about 9.0 kcal/mol of H-bonds at similar level of calculations [60]). Clearly, diaqua complexes of the Cu(I) cation represent the most stable form in water solutions. One particular detail deals with reduction of stabilization energy ($\Delta E^{Stab} - \Delta E^{Stex}$ is ca. $+3$ kcal/mol) when sterical repulsions are corrected in 3-coordinated $[Cu(H_2O)_6]^+$. This is caused by the fact, that not only sterical repulsions are subtracted in the used formula, but also attractive

Table 2
The stabilization energies of the Cu(I) and Cu(II) hydrates

| System	c.n.	ΔE^{Stab}	ΔE^{Stab}/n.w.	ΔE^{Stex}	ΔE^{coord}
$[Cu(H_2O)]^+$	1	41.8	41.8	42.1	41.8
$[Cu(H_2O)_2]^+$	2	84.1	42.1	86.2	42.1
$[Cu(H_2O)_3]^+$	2	101.4		102.8	41.6
	3	97.1	32.4	101.8	32.4
$[Cu(H_2O)_4]^+$	2	117.6		118.3	41.2
	3	112.0		114.5	31.1
	4	106.9	26.7	112.8	26.7
$[Cu(H_2O)_5]^+$	2	130.3		130.7	41.1
	3	125.8		128.0	30.9
$[Cu(H_2O)_6]^+$	2	142.2		142.0	41.1
	3	135.9		132.9	30.9
	4	132.9		135.8	25.3
$[Cu(H_2O)]^{2+}$	1	114.7	114.7	116.3	114.7
$[Cu(H_2O)_2]^{2+}$	2	205.8	102.9	209.0	102.9
$[Cu(H_2O)_3]^{2+}$	3	263.5	87.8	271.4	87.8
$[Cu(H_2O)_4]^{2+}$	4	306.7	76.7	322.8	76.7
$[Cu(H_2O)_5]^{2+}$	4	336.2		353.4	75.4
	5	334.0	66.8	354.3	66.8
$[Cu(H_2O)_6]^{2+}$	4	363.4		381.1	74.4
	5	358.6		380.2	65.7
	6	338.0	56.3	363.9	56.3

n.w., number of water molecules.
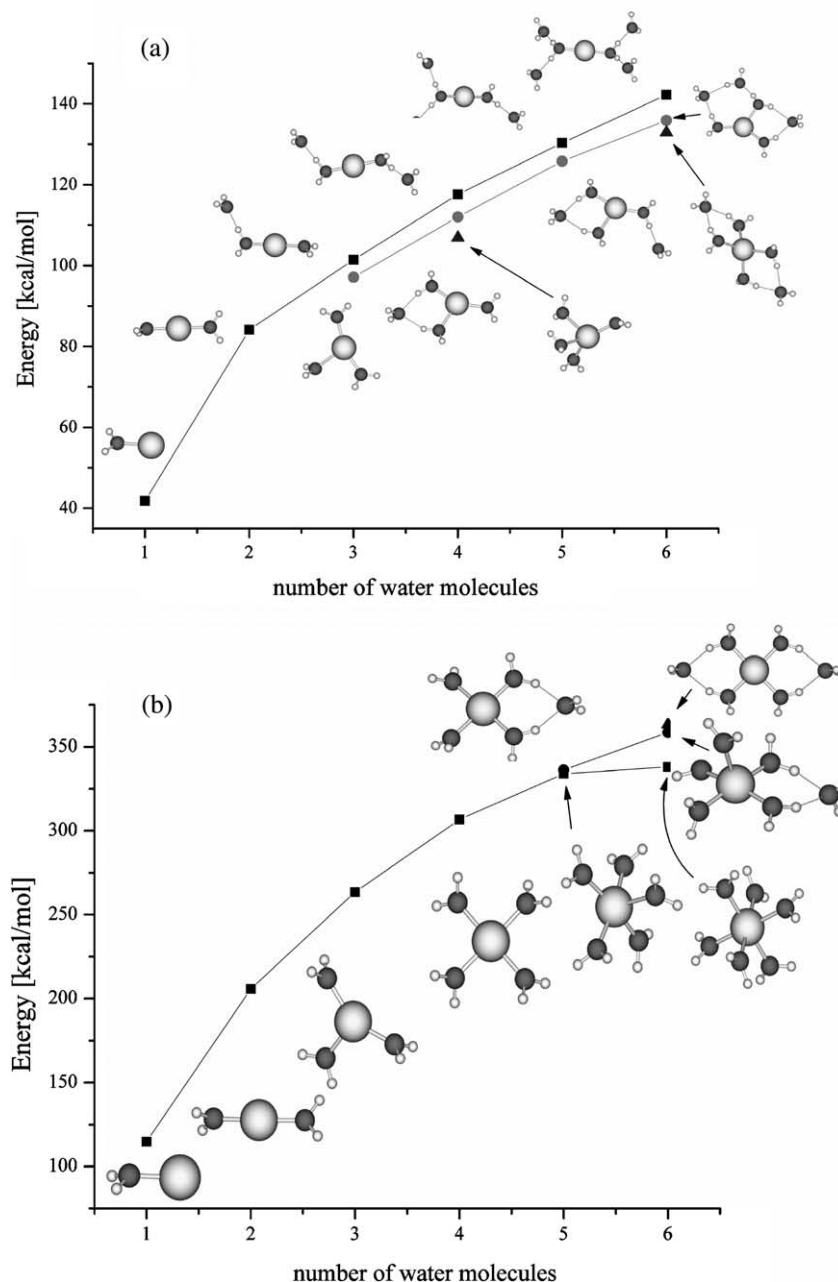
Fig. 3. (a) The stabilization energies of the Cu(I) systems. (b) The stabilization energies of the Cu(II) systems.

H-bonding interactions, which can prevail for weaker and lower coordinations when sufficient number of water molecules is present.

In the case of closed shell Cu(I) complexes, Morokuma's energy decomposition was performed to bring light in the bonding characteristics of the complexes. In Table 3a, one can clearly see that besides Coulomb interaction, polarization effects play very important role. Especially in case of 2-coordinated systems, polarization contributions are even larger than Coulomb energies. In $[Cu(H_2O)]^+$ case, small polarization leads to lower stabilization energy (see above). From the last column of Table 3a, it can be shown that the role of correlation contributions is also very important.

For instance, for systems with 6 waters, 4-coordinated structure has the largest interaction energy but the energy order is completely inverted when correlation effects are included. The same was found for stabilization energies ΔE^{Stab} at HF/6-311++G(2df,2pd)//HF/6-31+G(d) level where the 3-coordinated complexes were the most stable minima for 3, 4, and 5 watered systems and 4-coordinated complex in the case of 6 watered systems. The explanation insists mainly in exaggerated electrostatic and polarization contributions (not presented here). Only after inclusion of correlation contributions either at MP2 or B3LYP level, the correct energy order was obtained. In Table 3b, the extent of polarization on individual water molecules is demonstrated.

Table 3a
Morokuma's energy decomposition analysis for Cu(I) complexes

System	c.n.	E^{Elst}	E^{Ex}	E^{Pol}	$E^{CT+PL+X}$	ΔE^{HF}	ΔE^{MP2}
$[Cu(H_2O)]^+$	1	−59.08	45.70	−27.40	−22.93	−32.39	−9.03
$[Cu(H_2O)_2]^+$	2	−123.59	105.57	−201.46	−61.12	−62.93	−24.15
$[Cu(H_2O)_3]^+$	2	−153.16	132.10	−224.97	−78.71	−79.37	−28.47
	3	−142.19	102.01	−148.66	−52.44	−78.87	−22.27
$[Cu(H_2O)_4]^+$	2	−180.21	154.83	−244.17	−93.85	−95.09	−32.10
	3	−169.31	118.89	−128.20	−58.87	−94.93	−21.02
	4	−157.05	98.11	−84.21	−41.74	−92.27	−21.28
$[Cu(H_2O)_5]^+$	2	−200.93	168.02	−257.84	−101.47	−107.87	−34.71
	3	−193.07	138.33	−152.78	−71.48	−108.54	−28.07
$[Cu(H_2O)_6]^+$	2	−220.66	182.95	−271.62	−111.27	−119.56	−37.72
	3	−215.05	152.11	−118.23	−74.08	−119.95	−30.42
	4	−203.44	124.32	−56.55	−50.45	−120.70	−24.64

It is clearly seen that while directly coordinated waters exhibit relatively high polarization energy (more than 10 kcal/mol in 3-coordinated and even up to 30 kcal/mol in 2-coordinted complexes), polarization energy for the water molecules in second hydration shell is substantially reduced (below 5 kcal/mol). This also supports the conclusion from previous paragraph that additional water molecules will feel the influence of Cu(I) cation only marginally.

3.2.2. Cu(II) complexes

Despite a similar trend for Cu–O distances (the shortest bonds in diaqua followed by monoaqua complex) for both Cu(I) and Cu(II) cations, the stabilization energy related to number of Cu–O bonds ΔE^{Stab}/n.w. is larger in $[Cu(H_2O)]^{2+}$ than in corresponding diaqua system. On the contrary to structures containing hydrated Cu^+ cation, 4- (or maybe 5-) coordinated complexes are the most stable ones between all of the investigated hydrates of the Cu^{2+} ion. The stabilization energy behavior exhibits clear saturation for Cu(II) complexes (cf. Fig. 3b). In case of 5 and 6 watered complexes, one or two waters try to escape to second solvation shell. The stabilization energies for Cu^{2+} with 5 water molecules exhibit practical degeneracy for 4- and 5-coordinated complexes (difference 2 kcal/mol and about 3 kcal/mol if total energies are compared).

The inclusion of sterical repulsion corrections reverts the order, preferring 5-coordinated complex by about 1 kcal/mol. Thus, one can expect that the stability of both complexes will be very similar. When ZPVE corrections are calculated and entropy contributions evaluated, it can be found that the relative occurrence of 5-coordinated species according to Boltzmann law for Gibbs energy is about 9% at 298 K (in comparison with 0.2% for total energies). The same picture is also remarkable for Cu^{2+} systems with 6 water molecules. The differences in total and stabilization energies are slightly more pronounced—about 4 kcal/mol (ΔE^{Stab}(4-coord) − ΔE^{Stab}(5-coord)) and about 25 kcal/mol (ΔE^{Stab}(4–6)). The sterical-repulsion corrections decrease the differences to 1 and 16 kcal/mol. A smaller difference in ΔE^{Stex} energies can be explained by the fact that the higher is the coordination the larger sterical corrections occur.

Stabilization energy for $[Cu(H_2O)_6]^{2+}$ can be compared with formation energy published by Marini et al. [33] giving an excellent agreement (ca. 320 kcal/mol). Also Berces et al. [35] demonstrate very close stabilization of 4- and 5-coordinated structures for both penta- and hexa-aqua complexes. Their bonding energies: 90.8 (for triaqua), 78.6 (tetraaqua), 69.8, and 67.9 (4- and 5-coordinated pentaaqua), and 62.9, 61.9, 60.0 kcal/mol for hexaaqua complexes match very well with our results.

Table 3b
The decomposition of charge transfer + polarization energy for particular monomers

System	c.n.	Cu	$w1$	$w2$	$w3$	$w4$	$w5$	$w6$
$[Cu(H_2O)]^+$	1	−10.61	−12.32					
$[Cu(H_2O)_2]^+$	2	−29.77	−15.68	−15.68				
$[Cu(H_2O)_3]^+$	2	−33.10	−15.86	−24.53	*−5.21*			
	3	−22.71	−12.54	−11.52	−5.67			
$[Cu(H_2O)_4]^+$	2	−35.91	−24.10	−24.10	*−4.87*	*−4.87*		
	3	−21.61	−11.25	−8.55	−13.76	*−3.70*		
	4	−16.18	−6.80	−9.72	−4.12	−4.92		
$[Cu(H_2O)_5]^+$	2	−37.90	−27.84	−23.67	*−3.74*	*−3.74*	*−4.57*	
	3	−24.09	−14.08	−18.30	−7.89	*−3.48*	*−3.64*	
$[Cu(H_2O)_6]^+$	2	−40.37	−28.23	−28.23	*−3.67*	*−3.55*	*−3.67*	*−3.55*
	3	−22.42	−14.64	−14.06	−12.30	*−4.33*	*−3.18*	*−3.15*
	4	−14.10	−7.56	−7.56	−7.56	−7.56	*−3.05*	*−3.05*

All energies (in kcal/mol) are computed at RHF level for DFT structures; italics denotes water molecules in 2nd solvation shell.

Comparing stabilization energies of both cations, values for Cu(I) are markedly lower (more than twice) in comparison with Cu(II) complexes. This clearly shows that not only electrostatic interaction (twice higher charge) is stronger but also polarization energy and covalent bonding with higher donation (cf. below in discussion of partial charges) have to play important role. This is in accord with Morokuma energy decomposition performed for Cu(I) complexes where the role of polarization energy was also clearly demonstrated.

Complexes with the same coordination can be compared when the total number of water molecules increases. Coordination energy ΔE^{coord} is reduced as a reaction on a geometry deviation from the optimal structure (without any water in second shell). Thus this energy mirrors the deformation effects of the inner part of complexes. The energy differences are relatively very small and converge quickly as can be noticed for 2-coordinated Cu(I) systems.

3.2.3. Charge distribution

In order to obtain a deeper insight to studied systems, Weinhold NPA [66] partial charges were calculated and analyses of MOs were performed. There is one MO of the non-bonding orbitals of water, which can take part in σ-dative coordination to metal cation. Based on symmetry condition, such an orbital will contain admixture of vacant atomic orbitals of Cu, predominately 4s. An interesting detail deals with longer Cu–O distances in both Cu(I)/Cu(II) in monoaqua than in diaqua complexes. While in $[Cu(H_2O)]^{n+}$ complexes, admixture of Cu 4s AO exists in 8th MO in Cu^+ (see the MO in Fig. 4a) and 8th(alpha)/7th(beta) in Cu^{2+} case, two analogous MOs exist in $[Cu(H_2O)_2]^{n+}$ structure. The latter MOs exhibit substantially larger expansion coefficients of 4s (higher donation) which

corresponds to ca. 0.3e from both oxygens (cf. 7th and 11th MOs for $[Cu(H_2O)_2]^+$ in Fig. 4b and c; analogous orbital in Cu^{2+} are the 7th and 12th(alpha)/13th(beta) MOs). These orbitals demonstrate existence of substantially stronger dative bonds in diaqua complexes. This also corresponds to higher polarization energies found in Morokuma's decomposition for Cu^+ complexes.

Besides MO characteristics, occupation of individual valence atomic orbitals of Cu cation can be used for the quantification of donation effects, especially the occupation of 4s AO. In Table 4 occupations of 4s and 3d valence orbitals of copper cations are collected.

In case of Cu(I) complexes, it can be noticed that the highest donation occurs in cases of 2-coordinated structures. This is in accord with stabilization energies of these complexes. Also, the increasing donation passing from two interacting waters to six molecules gives another explanation why the 2-coordinated complex is the strongest between systems with six waters. In the higher part of Table 5, NBO partial charges of heavy elements of Cu(I) are present. As mentioned above, Cu charge deviates only slightly from $1+$ in monoaqua complex pointing on small electron density changes upon single water interaction as discussed above. Charge densities on O–H bonds of the coordinated waters are decreased due to H-bonding with second hydration shell, which leads to higher (more negative) partial charges on the donating oxygens. Higher charges on directly coordinated oxygens are visible in Table 5. Waters from second shell exhibit much smaller deviation from electron distribution in isolated water.

In Cu(II) systems, the situation is slightly more complicated since some donation can cause increased occupation of SOMO, cf. lower part of Table 4. Since some additional density appears in SOMO, only the partial
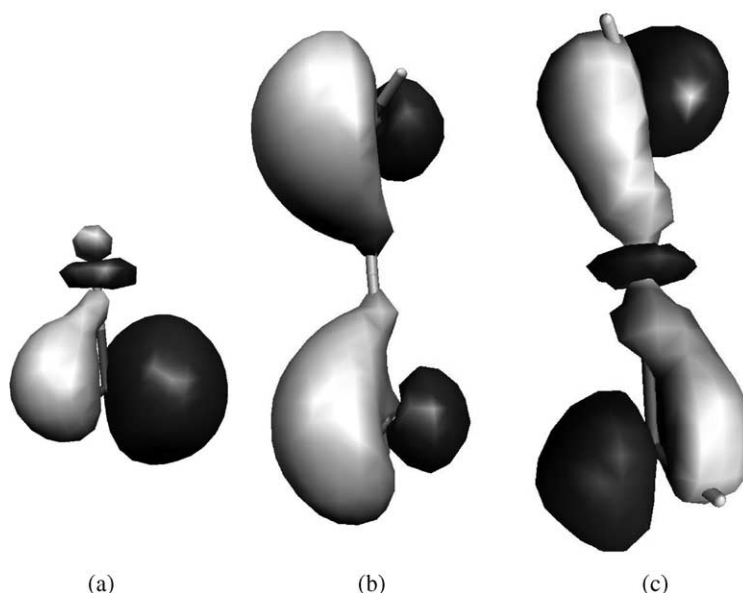

Fig. 4. MO involved in water donation: (a) 8th MO of $[Cu(H_2O)]^+$ (b) 7th MO of $[Cu(H_2O)_2]^+$ (c) 11th MO of $[Cu(H_2O)_2]^{2+}$.

Table 4
The occupation of some valence Cu AO

System		4s	3dx2y2	3dz2
$[Cu(H_2O)]^+$	1	0.102	2.000	1.941
$[Cu(H_2O)_2]^+$	2	**0.338**	1.872	1.957
$[Cu(H_2O)_3]^+$	2	**0.385**	1.931	1.950
	3	0.261	1.941	1.954
$[Cu(H_2O)_4]^+$	2	**0.411**	1.898	1.988
	3	0.242	1.967	1.948
	4	0.190	1.961	1.981
$[Cu(H_2O)_5]^+$	2	**0.431**	1.876	1.973
	3	0.271	1.928	1.951
$[Cu(H_2O)_6]^+$	2	**0.453**	1.843	1.952
	3	0.234	1.965	1.947
	4	0.144	1.988	1.995
$[Cu(H_2O)]^{2+}$	1	0.069	1.999	1.201
$[Cu(H_2O)_2]^{2+}$	2	0.164	1.776	1.379
$[Cu(H_2O)_3]^{2+}$	3	0.223	1.202	1.976
$[Cu(H_2O)_4]^{2+}$	4	0.241	1.241	1.978
$[Cu(H_2O)_5]^{2+}$	4	0.250	1.228	1.975
	5	0.233	1.184	1.982
$[Cu(H_2O)_6]^{2+}$	4	0.261	1.244	1.974
	5	0.241	1.216	1.985
	6	0.236	1.434	1.790

charges represent the unique criterion for donation extent. From the lower part of Table 5, it is evident that the smallest positive Cu partial charge is in the four-coordinated structure tightly followed by 5-coordinated (especially in the case of system with six water molecules). This means the largest electron donation occurs in these complexes. The strong donation correlates with the largest stabilization energies of these 4-(5-)coordinated complexes.

4. Conclusions

Optimizations of the complexes containing Cu^+/Cu^{2+} cations with varying number of water molecules (from one to six) were done using DFT method with B3PW91 functional.

It was found that the most stable structures with Cu^+ cation have only two coordinated water molecules.

Table 5
The NPA partial charges of the Cu and O atoms

System	Coord.	Cu	O1	O2	O3	O4	O5	O6
$[Cu(H_2O)]^+$	1	0.96	−1.03					
$[Cu(H_2O)_2]^+$	2	**0.83**	−0.98	−0.98				
$[Cu(H_2O)_3]^+$	2	**0.81**	−0.97	−1.01	*−0.95*			
	3	0.86	−0.98	−0.99	−0.99			
$[Cu(H_2O)_4]^+$	2	**0.80**	−1.01	−1.01	*−0.96*	*−0.96*		
	3	0.87	−0.98	−1.01	−1.01	*−0.97*		
	4	0.88	−0.99	−0.98	−0.99	−0.99		
$[Cu(H_2O)_5]^+$	2	**0.78**	−1.00	−1.03	*−0.96*	*−0.96*	*−0.96*	
	3	0.86	−1.01	−1.00	−1.01	*−0.96*	*−0.97*	
$[Cu(H_2O)_6]^+$	2	**0.77**	−1.02	−1.02	*−0.96*	*−0.95*	*−0.95*	*−0.96*
	3	0.87	−1.00	−1.01	−1.04	*−0.97*	*−0.97*	*−0.97*
	4	0.89	−1.00	−1.00	−1.00	−1.00	*−0.97*	*−0.97*
$[Cu(H_2O)]^{2+}$	1	1.72	−0.91					
$[Cu(H_2O)_2]^{2+}$	2	**1.69**	−1.01	−1.01				
$[Cu(H_2O)_3]^{2+}$	3	**1.59**	−0.99	−0.99	−1.00			
$[Cu(H_2O)_4]^{2+}$	4	**1.56**	−0.99	−0.99	−0.99	−0.99		
$[Cu(H_2O)_5]^{2+}$	4	**1.54**	−1.00	−0.99	−0.99	−0.99	*−0.98*	
	5	1.58	−1.02	−0.99	−0.98	−0.99	−0.98	
$[Cu(H_2O)_6]^{2+}$	4	**1.56**	−1.01	−1.00	−0.99	−0.99	*−0.98*	*−0.98*
	5	1.56	−1.00	−0.99	−0.99	−1.01	−0.98	*−0.98*
	6	1.64	−1.00	−0.98	−1.00	−1.01	−0.98	−1.01

$\delta(O)$, −0.93 for isolated water. Italics denotes oxygen from water molecules in 2nd solvation shell.

The other molecules prefer to stay in the second hydration shell. This is not the case of Hartree-Fock calculations where 3-coordinated (or 4-coordinated in $[Cu(H_2O)_6]^+$ case) complexes represent the most stable structures. An explanation of this fact can be seen in overestimated role of electrostatic and polarization contributions to total energies. More sophisticated methods, which include correlation effects (MP2, DFT) correct this artifact.

The most stable coordination for Cu^{2+} complex is four or maybe five. Both these coordinations exhibit similar stabilization energies especially when mutual repulsion of ligands is excluded. This is in very good accordance with experimental observations published in Ref. [65].

Stabilization energies with and without sterical corrections were determined for all complexes. With increasing number of coordinated molecules, the repulsion is increasing up to 30 kcal/mol in case of the 6-coordinated Cu^{2+} complex. The difference is substantially smaller for Cu^+ systems (e.g. 6 kcal/mol in case of the 4-coordinated complex). Morokuma's energy decomposition enlightens the importance of individual contributions. It is shown that at the Hartree-Fock level Coulomb and polarization terms predominate as one could expect for charged systems with metal cation.

Occupation of valence AOs (especially to 4s orbital) on Cu^+ cation points to the extent of water ligands donation. In case of Cu^{2+} complexes, partial charges (based on NBO analysis) could be used for illustration of donation effects. Analysis of MOs was used to explain differences in donation of monoaqua and diaqua complexes.

Acknowledgements

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