The influence of the Jahn–Teller effect and of heteroligands on the reactivity of Cu^{2+}†

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Experimentally hardly accessible Jahn–Teller inversions and the influence of heteroligands on the reactivity of Cu^{2+} are characterized by *ab initio* QM/MM MD simulations of Cu^{2+} ion and its amino complexes in water.

The Jahn–Teller distorted[1] hydrated Cu^{2+} complex is of special interest for structural as well as dynamical investigations.[2,3] Recently, computer simulations have become a powerful tool to reveal structural and dynamical properties of hydrated metal ions. A hybrid quantum mechanical/molecular mechanical (QM/MM)[4–6] method is the most appropriate way to avoid the problems of creating approximative multibody terms, keeping computational efforts still within feasibility. The QM/MM MD simulations include many-body terms in the most relevant part of the system (first hydration shell) using the unrestricted Hartree–Fock (UHF) method with double-zeta plus polarization functions basis sets[7,8] Comparison with DFT methods has shown that the BLYP functional of Car-Parinello simulations is rather inadequate for hydrated ions,[3,9–11] while the UB3LYP hybrid functional gives results very similar to the HF method, although with slightly too rigid structures and without gaining computational speed.[12] As HF QM/MM MD simulations where the MM part is described by *ab initio* generated pair potentials using the same basis sets as in the QM region have proven to be suitable to describe structural and dynamical properties of solvated ions[12] they were now extended to solvated complexes. All quantum mechanical calculations reported here were performed with a parallel implementation of TURBOMOLE 5.1.[13]

In this work QM/MM MD simulations of four different model systems were performed, consisting of 499 solvent molecules and 1 Cu^{2+} ion or, in order to evaluate the influence of heteroligands, Cu^{2+}(NH$_3$) and Cu^{2+}(NH$_3$)$_2$ with ligands in *cis* and *trans* positions. The main motivation of this work was to resolve inconsistencies concerning the coordination number of Cu^{2+} in water,[14] to obtain detailed information about the dynamic Jahn–Teller effect and to investigate the influence of heteroligand substitution in the first coordination sphere on the structural and dynamical properties of the ion in solution.

To analyse the hydration structure of Cu^{2+} and its amino complexes radial distribution functions (RDFs) and coordination number distributions (CNDs) were evaluated (see Table 1). The Cu–O RDFs depicted in Fig. 1 clearly show an increasing structural deformation of the first shell due to the heteroligands. [Cu(H$_2$O)$_6$]$^{2+}$ (Fig. 1(a)) shows a well-defined structure exhibiting a Jahn–Teller distortion (weak shoulder of the asymmetric first peak at 2.17 Å) with a constant first-shell coordination number of 6.

One heteroligand in the first shell leads to a broader and strongly tailed first shell peak (Fig. 1(b)) extended to 3.1 Å. Two shoulders in this peak correspond to more distant ligands in the distorted complex, including the intermediate sevenfold-coordinated [Cu(H$_2$O)$_6$(NH$_3$)]$^{2+}$ (~ 6%).
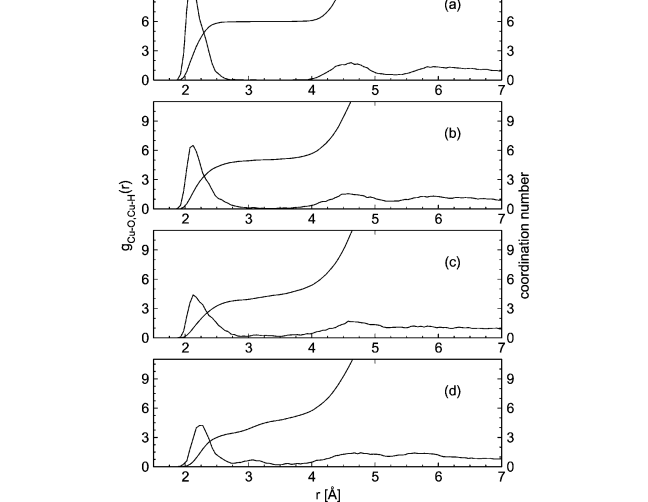
A second ammonia ligand strongly amplifies the observed effects. The Cu–O RDF of the *cis*-diamino complex (Fig. 1(c))

shows a strongly tailed broad first-shell peak and an additional inter-shell peak located at 3.12 Å. The first shell hydration numbers lie between 4 and 6, with an average value of 4.4 proving the sixfold-coordinated complex still to be dominant. The Cu–O RDF of the *trans*-diamine complex (Fig. 1(d)) shows by far the longest Cu–O bonds (2.28 Å) and exhibits a well defined peak between the first and second hydration shells. The average first shell coordination number of the hydrate complex with two *trans*-located heteroligands is 4.6 proving the preference for the sevenfold-coordinated [Cu(H$_2$O)$_5$(NH$_3$)$_2$]$^{2+}$ complex (~ 55%).

The very high lability of [Cu(H$_2$O)$_6$]$^{2+}$ is attributed to the dynamical Jahn–Teller effect causing the tetragonal bipyramidal distortion of the hydrated Cu^{2+} ion to randomly reorientate. Elongation of bonds to mostly *trans*-positioned

Table 1 Comparison of the most important structural and dynamical parameters obtained from QM/MM MD simulations of Cu^{2+} and its mono- and diamine complexes in water

	Pure water	Monoamine	*cis*-Diamine	*trans*-Diamine
$r_{1,max}$/Å^a	2.07/2.17	2.13	2.13 (3.12)	2.28 (3.07)
$r_{2,max}$/Å^a	4.62	4.58	4.58	4.78
CN-1$^{st\,b}$	6.0	5.1 (5–6)	4.4 (4–6)	4.6 (4–6)
CN-2$^{nd\,b}$	11.7 (7–15)	12.9 (9–18)	14.0 (8–19)	14.1 (8–19)
τ_{MRT} 1st/ps^c	230	115	75	35
τ_{MRT} 2nd/ps^c	23	21	21	20
Q_{iO}/cm$^{-1\,d}$	303 (180)^e	255	165 (270)	205

^{a} First/second peak maximum of Cu^{2+}–O RDF; numbers in parentheses correspond to small inter shell peaks. ^{b} First/second shell coordination number; numbers in parentheses correspond to the coordination number distributions. ^{c} First/second shell mean residence time. ^{d} Stretching mode of the ion–oxygen motion. ^{e} Number in parentheses corresponds to the shoulder caused by the Jahn–Teller effect.

Fig. 1 Cu–O radial distribution functions (RDFs) with their running integration numbers: QM/MM MD simulation of: (a) hexahydrate, (b) monoamine, (c) *cis*-diamine and (d) *trans*-diamine complex.

† Electronic supplementary information (ESI) available: QM/MM MD simulation; simulation protocol. See http://www.rsc.org/suppdata/cc/b3/b301709e/
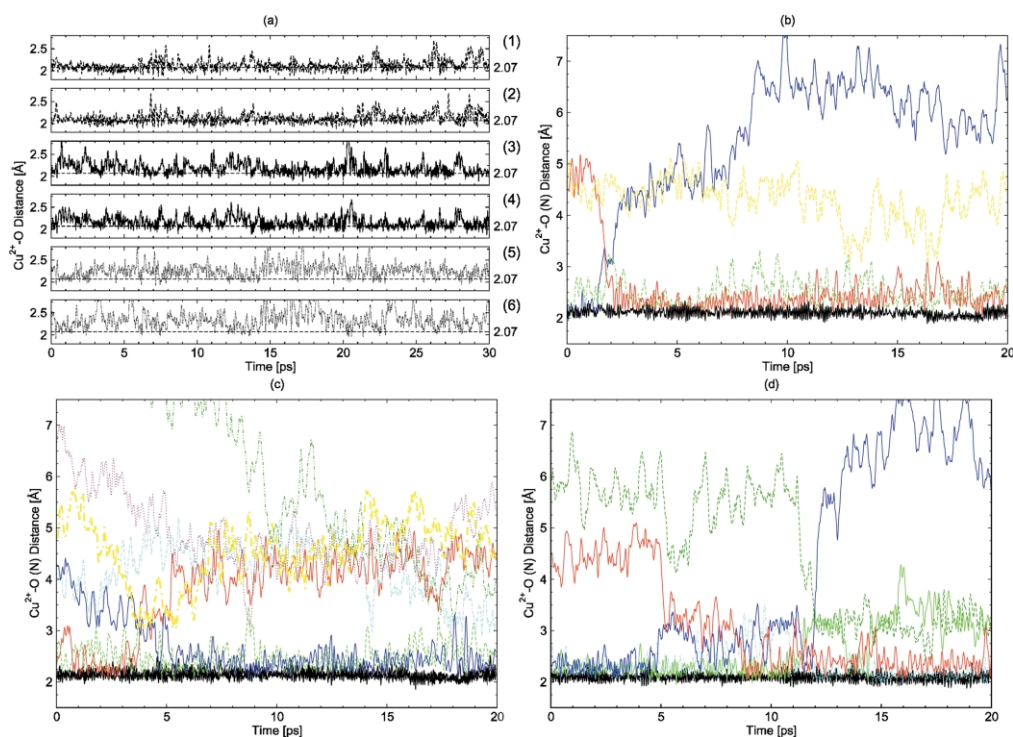
Fig. 2 Variation of the Cu–O (and Cu–N) distance(s) during the QM/MM MD simulations of (a) hexahydrate, (b) monoamine, (c) *cis*-diamine and (d) *trans*-diamine. (The bold lines show the variation of the Cu–N distances.)

H_2O molecules leads to an unusually fast water exchange compared to other transition metal ions. ^{17}O-NMR was used to estimate the inversion time of the Jahn–Teller distortions as well as water exchange times yielding values of ~5 ps for inversions and 230 ps for water exchanges.[15] Experiments have shown that in the cases of Cu^{2+} [16] and Ni^{2+} [17] increasing numbers of good electron donating ligands such as NH_3 lead to a nearly linear acceleration of the water exchange rate.

Fig. 2 summarizes the Cu–O(N) distance plots during the simulation times of 30 ps for Cu^{2+} in water and 20 ps for solvated amino complexes. In the case of $[Cu(H_2O)_6]^{2+}$ no first shell exchange was observed during the simulation time (Fig. 2(a)) but three pairs of opposite ligands ((1)–(2), (3)–(4), (5)–(6)) can be identified, often undergoing simultaneously Jahn–Teller distortions. The results clearly suggest that a time range of <200 fs is characteristic for the Jahn–Teller inversions. A further analysis shows that the distortions do not always only involve *trans*-located ligands and that sometimes more than two ligands are at elongated distances.

The presence of one NH_3 ligand molecule in the first coordination shell is sufficient to shift the time scale of the water exchange processes to that of the simulations performed. According to Fig. 2(b)–(d) in all heteroligand-containing complexes several first-shell water exchange processes are observed within 20 ps. The plots for the two diamine complexes impressively show the high stability of the sevenfold-co-ordinated species. At the same time, the Cu–N bond variations demonstrate the strength and rigidity of these bonds.

The calculation of mean residence times using the algorithm proposed by Impey[18] gives a quantitative measure for the heteroligand-induced labilization. A nearly linear enhancement of water exchange rates with increasing number of hetero-ligands is observed, and the relative position of the second heteroligands has a significant influence on the exchange rate (see Table 1). However no heteroligand effects are recognized in the second shell residence times. Ion–oxygen frequencies and the corresponding force constants supply indications about the strength of ligand binding (Table 1) showing a remarkable weakening of the Cu–O bond by one and two NH_3 molecules, respectively. The acceleration of water exchange processes by a factor of ~2 (1 NH_3), ~3 (*cis*) and ~6.5 (*trans*) is in good agreement with the changes in ion–oxygen frequencies.

The results obtained in this work appear of considerable interest, being a model case for Cu^{2+} coordinated to N-sites in biomolecules, where such coordination could strongly enhance the reactivity of the copper ion due to a facilitated exchange of water by other ligands.

Notes and references

1 I. B. Bersuker, *Chem. Rev.*, 2001, **101**, 1067.
2 L. Curtiss, J. W. Halley and X. R. Wang, *Phys. Rev. Lett.*, 1992, **69**, 2435.
3 H. Ohtaki and T. Radnai, *Chem. Rev.*, 1993, **93**, 1157.
4 A. Warshel and M. Levitt, *J. Mol. Biol.*, 1976, **103**, 227.
5 M. J. Field, P. A. Bash and M. Karplus, *J. Comput. Chem.*, 1990, **11**, 700.
6 J. Gao, in *Reviews in Computational Chemistry*, ed. K. B. Lipkowitz and D. B. Boyd, VCH Publishers, New York, 1996, vol. 7, ch. 3, pp. 119–185.
7 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.
8 T. H. Dunning Jr., *J. Chem. Phys.*, 1970, **53**, 2823.
9 I. Bakó, J. Hutter and G. Pálinkás, *J. Chem. Phys.*, 2002, **117**, 9838.
10 C. F. Schwenk, H. H. Loeffler and B. M. Rode, *J. Chem. Phys.*, 2001, **115**, 10808.
11 C. F. Schwenk, H. H. Loeffler and B. M. Rode, *Chem. Phys. Lett.*, 2001, **349**, 99.
12 B. M. Rode, C. F. Schwenk and A. Tongraar, *J. Mol. Liquids*, 2003, in press.
13 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165.
14 A. Pasquarello, I. Petri, P. S. Salmon, O. Parisel, R. Car, É. Tóth, D. H. Powell, H. E. Fischer, L. Helm and A. Merbach, *Science*, 2001, **291**, 856.
15 D. H. Powell, L. Helm and A. E. Merbach, *J. Chem. Phys.*, 1991, **95**, 9258.
16 I. Nagypál and F. Debreczeni, *Inorg. Chim. Acta*, 1984, **81**, 69.
17 A. G. Desai, H. W. Dodgen and J. P. Hunt, *J. Am. Chem. Soc.*, 1970, **92**, 798.
18 R. W. Impey, P. A. Madden and I. R. McDonald, *J. Phys. Chem.*, 1983, **87**, 5071.