



# Structure and dynamics of $[\text{CuCl}_n(1,2\text{-diaminoethane})]$ complexes in aqueous solution by Quantum Chemistry and Molecular Dynamics methods

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## Introduction

Over the past decades, transition metal complexes have attracted considerable attention in medicinal inorganic chemistry, especially as synthetic metallonucleases and metal-based anticancer drugs that are able to bind to DNA molecules under physiological conditions. The use of metal-based drugs presents the most important strategy in the development of new anticancer and antimicrobial agents [1]. The present study is focused on structure and dynamics of  $[\text{CuCl}_n(1,2\text{-diaminoethane})]$  complex (labeled henceforth as  $[\text{CuCl}_n(\text{en})]$ ) in aqueous solution using quantum chemistry calculations and molecular dynamics simulation.

## Methods

A set of three complexes ( $[\text{CuCl}_2(\text{en})]$ ,  $[\text{CuCl}(\text{en})]^{1+}$  and  $[\text{Cu}(\text{en})]^{2+}$ ) in aqueous environment was modeled by restricted Hartree-Fock method using GAMESS program [2]. The calculations were performed in the basis set CCT (cc-pVTZ [3]) with multiplicity 2. Initial configuration of the isolated electrically neutral  $[\text{CuCl}_2(\text{en})]$  complex was optimized in vacuo. Its optimized structure is shown in Fig. 1. The coordination of copper ion is tetrahedral. This configuration was taken as initial for the simulations of complexes with water.

## Results

Adding water molecules (up to 10) leads to 5-coordinated copper ion (see Fig. 2, only water molecules in the first hydration shell of copper ion are shown for clarity) independently on their initial positions and number. Dissociation of  $\text{CuCl}_2$  was not observed. Double charged system  $[\text{Cu}(\text{en})]^{2+}$  in aqueous environment tends to form 6-coordinated ion complex (Fig. 3). Single charged  $[\text{CuCl}(\text{en})]^{1+}$  in aqueous environment tends to build 6-coordinated ion complex in two ways (Fig. 4a, 4b). Results of quantum chemical calculations are summarized in Table 1.

Aqua complex	N	Cl	H <sub>2</sub> O	Structure
$[\text{Cu}(\text{en})]^{2+}$	2	-	4	octahedron
$[\text{CuCl}(\text{en})]^{1+}$	2	1	3	octahedron
$\text{CuCl}_2(\text{en})$	2	2	1	5-coordinated

Table 1: Number of atoms in the first coordination shell of copper ion for the investigated aqua complexes

## Molecular dynamics modeling

The molecular dynamics simulations of infinitely dilute aqueous solution of 1,2-diaminoethane and  $\text{CuCl}_2$  were carried out. Structural and dynamical characteristics (radial distribution functions, lifetime of water molecules in the hydration shell of the ion, coordination number of the ion, and other parameters) of the system were analyzed.

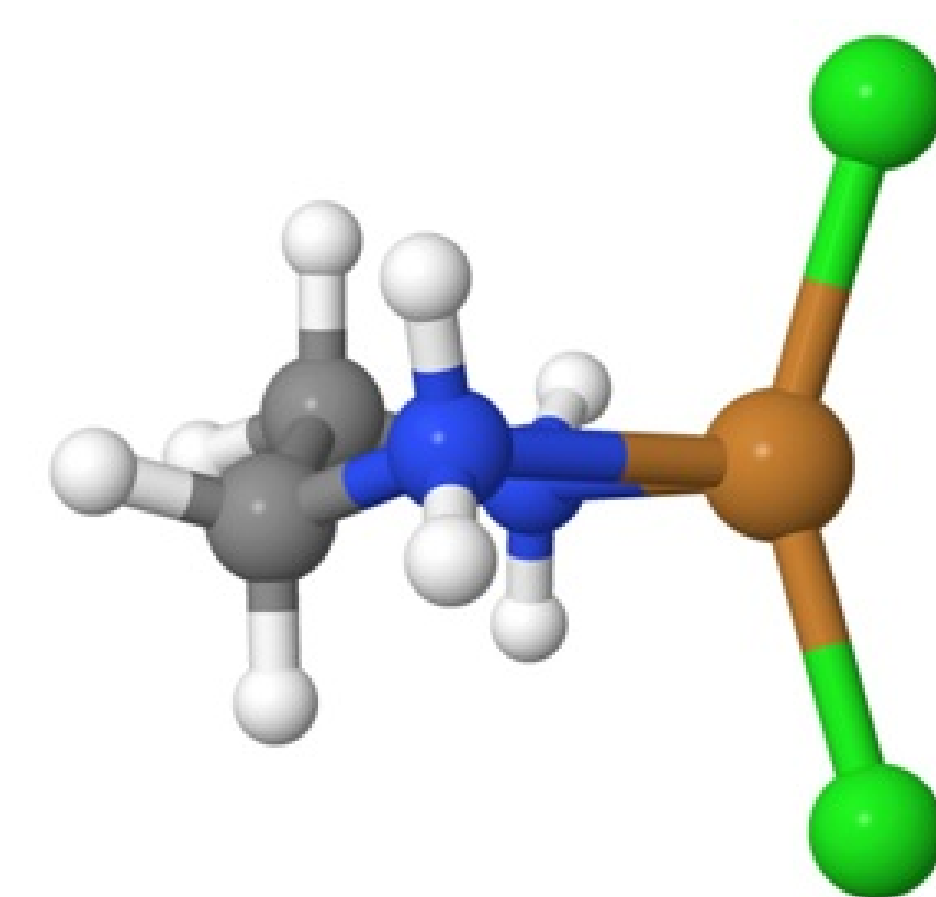


Fig. 1. The optimized structure of  $[\text{CuCl}_2(\text{en})]$  complex in vacuo

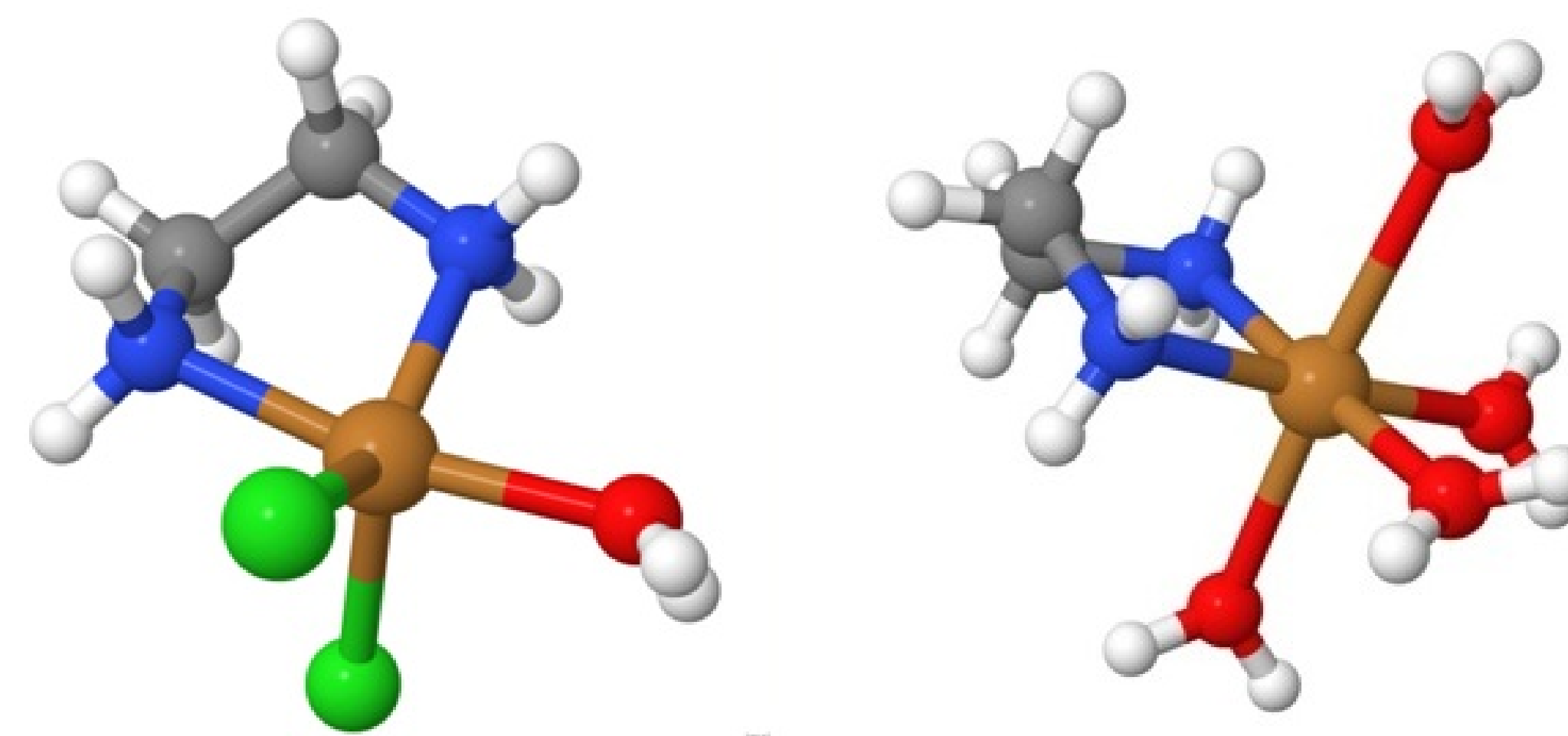


Fig. 2.  $[\text{CuCl}_2(\text{en})]$  aqua complex Fig. 3.  $[\text{Cu}(\text{en})]^{2+}$  aqua complex

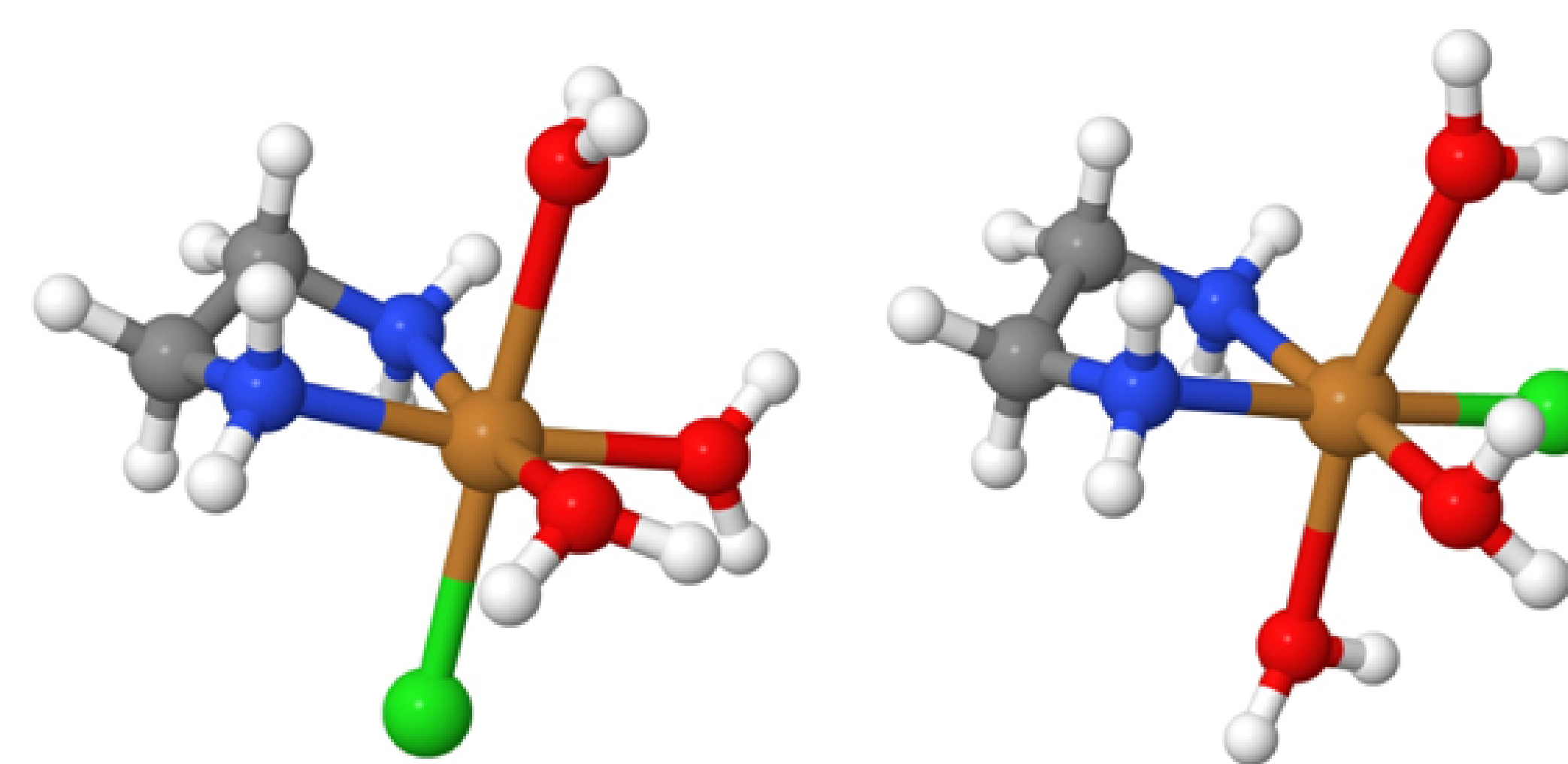


Fig. 4(a, b). The optimized structures of  $[\text{CuCl}(\text{en})]^{1+}$  aqua complexes

## References

- [1] E. Selimović, A. V. Komolkin, A. V. Egorov, T. Soldatović, «Substitution behavior of square-planar and square-pyramidal  $\text{Cu}(\text{II})$  complexes with bio-relevant nucleophiles», *J. Coord. Chem.*, 71, 1003 (2018).
- [2] M. S. Gordon, M. W. Schmidt. In book: «Theory and Applications of Computational Chemistry, the first forty years», C. E. Dykstra, G. Frenking, K. S. Kim, G. E. Scuseria (editors). – Elsevier, Amsterdam, 2005. Pages 1167-1189.
- [3] N. B. Balabanov, K. A. Peterson, «Systematically convergent basis sets for transition metals. I. All-electron correlation consistent basis sets for the 3d elements  $\text{Sc-Zn}$ », *J. Chem. Phys.*, 123, 064107 (2005).