Two possible bis(glycinato)copper(II) isomerization mechanisms - theoretical predictions

Vjeran Gomzi

Division of Organic Chemistry and Biochemistry / Quantum Organic Chemistry Group, Rudjer Boskovic Institute, Zagreb, Croatia
e-mail: vgomzi@irb.hr

The interactions with water medium during cis-trans bis(glycinato)copper(II) isomerization modeled either by adding water molecules explicitly or through the Polarized Continuum Model (PCM) have been investigated by Density Functional (B3LYP) method. The crucial dependence of theoretical energies on the accuracy of PCM corrections has been established. It has been shown that for the bis(glycinato)copper(II) the differences of isomer energies are of the order of the PCM corrections' reliability limit. On the basis of calculation results two possible mechanisms for the cis-trans isomerization have been proposed. It was shown that only the inclusion of two explicit water molecules enables the modeling of the isomerization mechanism involving the interchange of glycine and water oxygen atoms in copper coordination. Involvement of ligand water in this mechanism is found to significantly lower the cis-trans barrier energy. The other proposed mechanism involves transient complex reduction. This mechanism has also been found energetically feasible, with barrier energy of the order of 51 kJ/mol and 107 kJ/mol, depending on the estimation of Coulomb interaction energies between charged species. Significance of reduction-mediated isomerization is further supported by the change of the shape of HOMO in oxidized and reduced species and in the transition-state.