Kinetics and DFT Studies on the Reaction of Copper(II) Complexes Supported by \(N,N\)-Bis(2-quinolylmethyl)amine Tridentate Ligands toward \(H_2O_2\)

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Kinetics and DFT studies on the reaction of copper(II) complexes supported by bulky tridentate ligands \(L_1^R\) \((N,N\)-bis(2-quinolylmethyl)amine tridentate ligands) toward \(H_2O_2\) have been investigated in detail.

The copper(II) complexes exhibit a square pyramidal structure containing a coordinated solvent molecule at an equatorial position and a weakly coordinated counter anion (or water) at an axial position. They reacted readily with \(H_2O_2\) at a low temperature to give mononuclear hydroperoxo copper(II) complexes. Stopped-flow kinetics and DFT studies have suggested that, in the initial stage of the reaction, deprotonated hydrogen peroxide attacks the cupric ion, presumably from the axial position, to give a hydroperoxo copper(II) complex retaining the coordinated solvent molecule \((H^R\cdot S)\). \(H^R\cdot S\) then loses the solvent to give a tetragonal copper(II)-hydroperoxo complex \((H^R)\), in which the \(-OOH\) group may occupy an equatorial position (Scheme 1). The copper(II)-hydroperoxo complex \(H^R\) exhibits a relatively high O–O bond stretching vibration at 900 cm\(^{-1}\) compared to other previously reported examples.

\[ \text{Scheme 1.} \]

\[ \begin{align*}
\text{Sol} & \quad \text{ClO}_4^- & \quad \text{O} & \quad \text{OH} & \quad \text{Sol} \\
\text{Cul}^+ & \quad \text{N} & \quad \text{N} & \quad \text{N} & \quad \text{ClO}_4^- \\
\text{H}^R & \quad \text{R} & \quad \text{S} & \quad \text{Cul}^+ \\
\end{align*} \]