Density functional studies of the structural variety of the Cu₂S₂ core of the Cu_A site

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The Cu_A site is contained in cytochrome *c* oxidase (C*c*O), the terminal electron acceptor in aerobic respiration, and nitrous oxide reductase (N₂OR), the terminal acceptor in anaerobic respiration. It provides an appropriate electronic structure for rapid electron transfer. The X-ray crystallographic studies demonstrated that the Cu_A site is composed of two copper ions bridged with two bridging cystenyl thiolate groups, and that each copper ion is coordinated equatorially with a histidine residue and axially with either a methionine residue or a carbonyl group of the polypeptide backbone. We have studied the characteristic electronic structures of the Cu_A site and the effects of each coordinating amino acid on it [1, 2].

The X-ray crystal structures also showed that the structural variety of the Cu_2S_2 core of the Cu_A site with a short Cu–Cu distance of 2.35–2.59 Å and a S–S distance of 3.75–4.25 Å. In the present study, we address the origin of the structural variety of the Cu_2S_2 core of the Cu_A site, using the density functional theory. Our computation demonstrated that the Cu_2S_2 core itself cannot explain the structural variety, indicating the requirement of ligand coordination.

[1] Y. Takano, Y. Shigeta, K. Koizumi, H. Nakamura, *Int. J. Quantum Chem.* **2012**, *112*, 208–218.

[2] K. Koizumi, Y. Shigeta, O. Okuyama, H. Nakamura, Y. Takano, *Chem. Phys. Lett.* submitted.