Formation of “Bridged Butterfly Structures” in Reduction Steps of Dioxygen on Dicopper Complex Systems

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The metal-dioxygen adducts in active sites of non-heme diiron and dicopper proteins are formed by oxygenation of the reduced metal centers with molecular dioxygen. In general, the peroxo intermediates, $M_2(\mu\text{-}O_2)$ species, are given as the initial reaction intermediates, and high-valent $M_2(\mu\text{-}O)_2$ species are generated by way of the subsequent O-O bond cleavage in the further O_2-reduction steps.[1] Such the dioxygen activating metalloproteins often have pre-organized pseudo-tetrahedral coordination structures. We focused on this structural factor around the active metal cernters and introduced the pseudo-tetrahedral coordination into the biomimetic dinuclear metal complex systems activating molecular dioxygen.

In this study, we used a natural alkaloid, (-)-sparteine (**Sp**) and its stereoisomers (α-isosparteine (**α-Sp**) and β-isosparteine (**β-Sp**)) as bidentate ligands enforcing pseudo-tetrahedral coordination around the metal centers. X-ray studies of these copper complexes with **Sp** revealed that these copper centers have twisted coordination structures, due to the steric requirements of the ligand. The Cu^{I} complex with **Sp** rapidly reacted with molecular dioxygen to form the cooresponding $Cu^{III}_2(\mu\text{-}O)_2$ species in the organic solvents at –80 °C. These $Cu^{III}_2(\mu\text{-}O)_2$, with **Sp** exhibiting unique spectroscopic properties. The characteristic low-energy LMCT bands and high-energy resonance Raman frequencies for these $Cu_2(\mu\text{-}O)_2$ cores were systematically shifted due to changing stereoisomers of **Sp**. While, the Cu^{I} complex of **α-Sp** was oxygenated to form $Cu^{II}_2(\mu\text{-}\eta^2:\eta^2\text{-}O_2)$ species in the presence of bridging ligands, such as a benzoate. X-ray clearly revealed that this $Cu^{II}_2(\mu\text{-}\eta^2:\eta^2\text{-}O_2)$ complex with a benzoate had a “bridged butterfly structure”. Dissociation of the bridging ligand caused the second structural change to the corresponding $Cu^{III}_2(\mu\text{-}O)_2$ species. Such the bridged core structures must have strong relevancies to the precursor of high-valent O_2-activating intermediate in dimetal centers of biological systems.

[1] a) Wallar, B. J.; Lipscomb, J. D. *Chem. Rev.* **1996**, *96*, 2625. b) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. *Chem. Rev.* **2004**, *104*, 1013. c) Lewis, E. A.; Tolman, W. B. *Chem. Rev.* **2004**, *104*, 1047.