Electronic Structure of O_2-Bound Metal Sites in Biomimetic Model Complexes

Dioxygen is essential in life processes, and metalloenzymes activate dioxygen (O_2) to carry out a variety of biological reactions including biotransformation of naturally occurring molecules and oxidative metabolism of xenobiotics. One primary goal in biomimetic research is to understand the mechanistic details of dioxygen activation and oxygenation reactions and the structures of reactive intermediates formed at the active sites of the metalloenzymes.

A group of Ewha Womans University researchers, led by Prof. Nam, recently prepared a series of metal-O_2 intermediates as models of biological mononuclear active centers, which demonstrated biolgocially relevant small molecule catalysis. In biological systems, the metal site is held in place usually by protein-based ligands. O_2 can then approach and bind to the metal center for transfer to target areas or for activation for a reaction with a substrate. The protein-based ligands play a crucial role in stabilizing the metal center and the nature, type and number of these ligands can affect the metal-O_2 interaction strongly. The metal-O_2 systems prepared by Nam *et al.* have cyclic ligand systems with differing ring sizes. Although this difference is small, the effect of ring size on the metal-O_2 bonding appeared to be dramatic. In collaboration with researchers at Stanford University and SSRL, Nam *et al.* investigated the role of the ligand ring size in affecting the geometric and electronic factors that determine the final structure of these metal-O_2 complexes. They studied Ni-O_2 and CoO_2 complexes with 12-membered (12-TMC) and 14-membered (14-TMC) (Figure 1) ring ligands using x-ray absorption spectroscopy and EXAFS data collected on the two Structural Molecular Biology beamlines 7-3 and 9-3 at SSRL and combined it with DFT calculations.

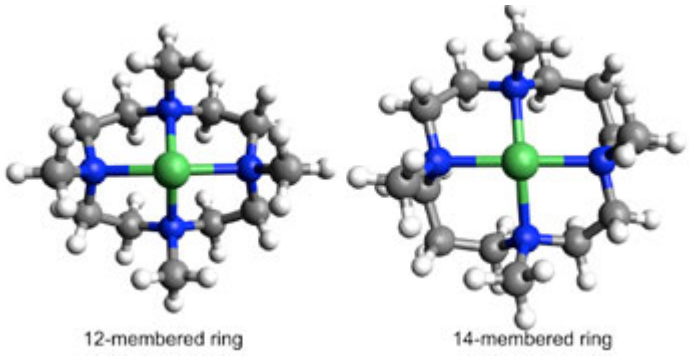

Figure 1 Schematic showing a central atom (Ni or Co) bound to a 12- and 14-membered ring ligand.

The study revealed that in the case of the O_2 bound Ni compounds, [Ni(12-TMC)-O_2] was a sideon bound Ni(III)-peroxide species, while the [Ni(14-TMC)-O_2] was an end-on bound Ni(II)-superoxide species. This difference in electronic and geometric structure was assigned on the basis of Ni K-edge XAS and EXAFS experiments (Figure 2). DFT calculations showed that these differences arise due to the differences in ring size. The 12-membered ring is constrained and can accommodate a tightly bound O_2 moiety, while the 14-TMC ring is more flexible and can only accommodate a weakly bound O_2.

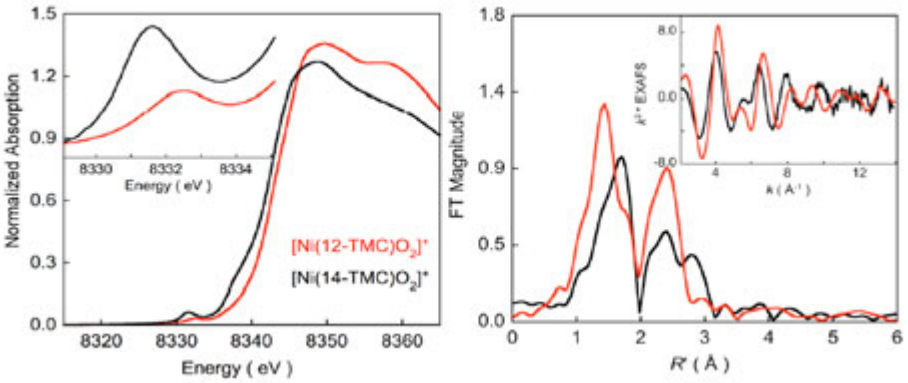

Figure 2 The normalized Ni K-edge XAS (inset shows the expanded pre-edge region) (left), EXAFS and their corresponding Fourier transforms (right) of $[Ni(12\text{-}TMC)O_2]^+$ and $[Ni(14\text{-}TMC)O_2]^+$. The shift in the edge energy positions and the difference in the EXAFS and Fourier transforms clearly indicate the differences in geometric and electronic structure.

A striking difference was observed in the comparison of the $[Co(12\text{-}TMC)O_2]^+$ and $[Co(14\text{-}TMC)O_2]^+$ systems. Both molecules have a side-on bound Co(III)-peroxide electronic structures. The change in ring size did not affect the mode of binding or the redox state of the Co-O_2 moiety. However, the EXAFS reveal that the $[Co(14\text{-}TMC)O_2]^+$ molecule undergoes significant distortion to accommodate the side-on binding of the O_2 moiety (Figure 3). DFT calculations reveal that as a six-coordinate molecule $[Co(14\text{-}TMC)O_2]^+$, the stability of the Co(III) redox state over the Co(II) redox state wins over the sterics posed by the 14-TMC ring, leading to significant distortion in the ring to stabilize a Co(III) redox state. This results in a change in the spin state of the molecule; $[Co(12\text{-}TMC)O_2]^+$ is S=0, while $[Co(14\text{-}TMC)O_2]^+$ is S=1.

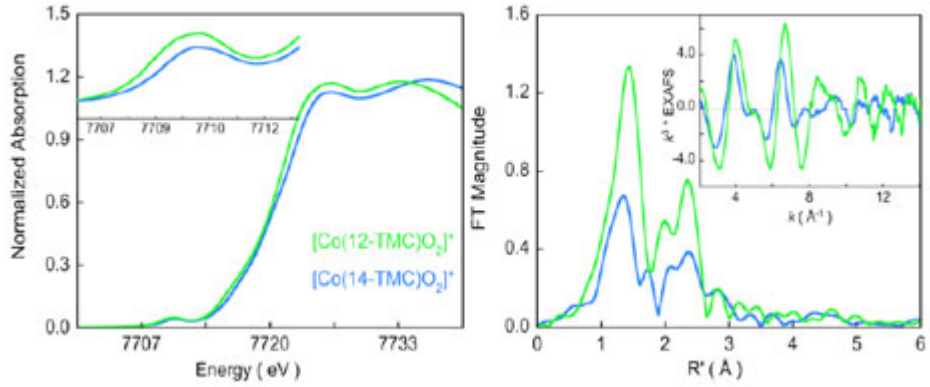

Figure 3 The normalized Co K-edge XAS (inset shows the expanded pre-edge region) (left), EXAFS and their corresponding Fourier transforms (right) of $[Co(12\text{-}TMC)O_2]^+$ and $[Co(14\text{-}TMC)O_2]^+$. The similarity of the edge energy positions and the dramatic decrease in the EXAFS and Fourier transforms clearly indicate that the Co is Co(III) in both species, but the ring has undergone significant rearrangement.

The study was able to show that there is interplay of different factors including the relative stability of the metal site and the ligand sterics and electronics in determining the final mode of binding of O_2 to the metal center. Importantly, the study indicates that the binding of O_2 to biological metal centers is a complex combination of factors and each metal-ligand system should be individually evaluated for the type of metal-O_2 interaction in order to evaluate O_2 binding and activation. This study sheds light on two important metal centers and their coordination environments on the reactivity of the metal-O_2 intermediates. These studies on metal-O_2 intermediates have implications not only in the biological systems where metalloenzymes activate O_2 for reactivity but also in organic synthesis where these compounds can be used as oxidizing agents or as better industrial catalysts. These studies have been reported in three publications in *Nature Chemistry*, *J. Am. Chem. Soc* and in *Inorg. Chem.*

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Primary Citations

(1) Sarangi, R.; Cho, J.; Nam, W.; Solomon, E. I. *Inorg. Chem.* **2011**, *50*, 614.

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(3) Cho, J.; Sarangi, R.; Annaraj, J.; Sung Yeon, K.; Kubo, M.; Ogura, T.; Solomon, E. I.; Nam, W. *Nat. Chem.* **2009**, *1*, 568-572.