

Advances in Dinuclear Metal Complexes Containing Bulky Carboxylate Ligands

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Non-heme iron enzymes have received much interest due to their ability to activate dioxygen, and of these, several exhibit dinuclear iron active sites (MMOH, reduced form of ribonucleotide reductase, Δ^9 -desaturase). Solid state structures reveal the presence of six conserved residues, four carboxylate and two nitrogen donor ligands. The observed binding modes of the carboxylate ligands in these enzymes are diverse, and illustrate the importance of the carboxylate functionality in accommodating subtle changes in the diiron coordination environment.

Model complexes containing bulky benzoate ligands (dmbCO_2^- and dxlCO_2^-) have given insight into the solid state and solution structures of dinuclear iron complexes which possess structures similar to that observed in the natural enzymes. These diiron complexes have been shown to react with molecular oxygen and exhibit spectroscopic features that indicate new and unusual coordination modes of the dioxygen to the diiron center. Efforts to more completely understand the oxygenation chemistry of metal complexes containing bulky carboxylate ligands have been explored and will be discussed.