Non-Heme Metal Thiolate Complexes of Novel NNO Phenolate Ligands and their Oxidation Chemistry

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Sulfur is a multivalent, soft ligand that enables a high degree of covalent character in the bonds it forms to transition metal centres. Indeed, the coordination of thiolates to iron is of crucial biological importance, facilitating complex electron transport mechanisms, the stabilisation of high metal oxidation states, and the lowering of the energetic activation barrier for O₂ binding. In this work, particular interest is given to *isopenicillin N synthase* (IPNS), a mononuclear non-heme enzyme that is capable of activating O₂ and whose native substrate (ACV; d-(L-a-aminoadipoyl)-L-cysteinyl-D-valine) binds to the active site by means of a single iron-sulfur bond (Figure 1) [1,2]. Moreover, IPNS displays unique reactivity in its ability to use the full 4-electron oxidising power of dioxygen for the double ring-closure of ACV to isopenicillin N (IPN), during which two aliphatic C-H bonds are activated and no sulfur oxygenation occurs.

Here we present novel tripodal NNO phenolate ligands DiPhImNNO that are able to structurally mimic the 2-His-1-carboxylate facial triad (2H1C), found at the active site of IPNS [1,3]. Their reaction with M(OTf)₂ salts (M = Fe²⁺, Zn²⁺) produces highly symmetrical dimers that serve as convenient synthons for terminal metal-thiolate complexes, whose dimeric structure remains intact (Figure 2). Current efforts are focused on identifying the manner in which oxidation occurs within these multi-redox-component complexes. In this vein, cyclic voltammetry is used to probe the electrochemical behaviour of the redox components, and chemical oxidants including oxo-transfer reagents are used to explore the oxidation chemistry of these complexes. Ultimately, this project aims to create novel structural and functional models of IPNS where selective C-H activation occurs in the presence of a sulfur-bound substrate.


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