Computational study of ligand oxidations of Ni and Zn complexes of N1,N9-bis(imino-2-mercaptopropane)-1,5,9-triazanonane

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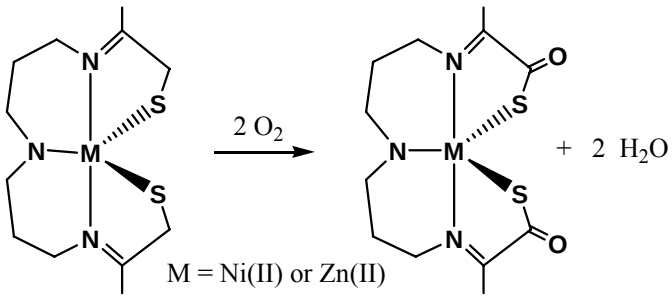

Low-spin nickel thiolate complexes generally react with oxygen forming sulfenates, sulfinates and sulfonates. Cysteine metabolism involves such sulfoxy species. While square planar low-spin Ni(II) thiolate complexes have been studied extensively and all undergo reactivity at the sulfur[1-3], a recently reported high-spin Ni(II) thiolate and the isostructural Zn(II) complex exhibit a different type of reactivity with oxygen.[4] The trigonal-bipyramidal Ni(II) or Zn(II) complexes of N1,N9-bis(imino-2-mercaptopropane)-1,5,9-triazanonane react with two molecules of oxygen forming a bis-iminothiocarboxylate via carbon oxidation. The reported activation parameters of the reaction ($\Delta G^{\ddagger}$) are 17.1 kcal/mol and 19.6 kcal/mol for the Ni and Zn complexes, respectively, at 298 K. The proposed reaction mechanism has been evaluated using hybrid density functional calculations. Pre-coordination of oxygen to the metal does not appear to be involved in the reaction. The reaction is initiated by nucleophilic attack by the complex HOMO (largely sulfur p-orbital based) with the LUMO of dioxygen, concurrent with abstraction of a C-H proton resulting in a thiohydroperoxide. Rearrangement to the C-OOH hydroperoxide is followed by O-O bond cleavage.

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