Title	Tuning Reactivity and Mechanisms of Oxidation with Nonheme Manganese(IV)-Oxo Complexes
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Abstract of Thesis

Name	(Heejung Yoon)
Title	Tuning Reactivity and Mechanisms of Oxidation with Nonheme Manganese(IV)-Oxo Complexes (ノンヘムマンガン(IV)-オキソ錯体の反応性制御と酸化反応機構)

Abstract of Thesis

In this thesis, tuning reactivity and mechanisms of oxidation with manganese(IV)-oxo complexes with pentadentate ligands has been focused. The factors that tune the redox reactivity of the oxo intermediates were thoroughly investigated especially with regard to the effects of Lewis acids (i.e., redox-inactive metal ions and proton) to the nonheme manganese(IV)-oxo moiety. In chapter 1, basic electron-transfer properties of a nonheme manganese(IV)-oxo complex have been investigated for the first time. In chapter 2, the mechanism of hydride transfer from NADH analogs to an nonheme manganese(IV)-oxo complex is compared with that of hydride transfer to an iron(IV)-oxo complex. In chapter 3, a mononuclear nonheme manganese(IV)-oxo complex binding redox-inactive scandium ion, $[(\mathrm{L})\mathrm{Mn}^{\mathrm{IV}}(\mathrm{O})]^{2+}{-}(\mathrm{Sc}^{3+})_2$, has been synthesized and characterized with various spectroscopic methods. The reactivities of the nonheme manganese(IV)-oxo complex in the absence and presence of scandium ions were studied in oxygen atom transfer (OAT) and hydrogen atom transfer (HAT) reactions. In chapter 4, the fundamental electron-transfer properties of $[(\mathrm{L})\mathrm{Mn}^{\mathrm{IV}}(\mathrm{O})]^{2+}{-}(\mathrm{Sc}^{3+})_2$ have been investigated to provide mechanistic insight into sulfoxidation by $[(\mathrm{L})\mathrm{Mn}^{\mathrm{IV}}(\mathrm{O})]^{2+}{-}(\mathrm{Sc}^{3+})_2$. In chapter 5, diprotonated nonheme manganese(IV)-oxo complexes, $[(\mathrm{L})\mathrm{Mn}^{\mathrm{IV}}(\mathrm{O})]^{2+}{-}(\mathrm{HOTf})_2$, were synthesized by adding HOTf (trifluoromethanesulfonic acid) to $[(\mathrm{L})\mathrm{Mn}^{\mathrm{IV}}(\mathrm{O})]^{2+}$ complexes and were characterized by various spectroscopic methods. The fundamental electron-transfer properties of $[(\mathrm{L})\mathrm{Mn}^{\mathrm{IV}}(\mathrm{O})]^{2+}{-}(\mathrm{HOTf})_2$ have also been investigated to compare the reactivities with OAT and HAT reactions.

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

In this thesis, tuning reactivity and mechanisms of oxidation with manganese(IV)-oxo complexes with pentadentate ligands has been focused. The factors that tune the redox reactivity of the oxo intermediates were thoroughly investigated especially with regard to the effects of Lewis acids (i.e., redox-inactive metal ions and proton) to the nonheme manganese(IV)-oxo moiety.

In chapter 1, basic electron-transfer properties of a nonheme manganese(IV)-oxo complex have been investigated for the first time. In chapter 2, the mechanism of hydride transfer from NADH analogs to an nonheme manganese(IV)-oxo complex is compared with that of hydride transfer to an iron(IV)-oxo complex. In chapter 3, a mononuclear nonheme manganese(IV)-oxo complex binding redox-inactive scandium ion, $[(L)Mn^{IV}(O)]^{2+}–(Sc^{3+})_2$, has been synthesized and characterized with various spectroscopic methods. The reactivities of the nonheme manganese(IV)-oxo complex in the absence and presence of scandium ions were studied in oxygen atom transfer (OAT) and hydrogen atom transfer (HAT) reactions. In chapter 4, the fundamental electron-transfer properties of $[(L)Mn^{IV}(O)]^{2+}–(Sc^{3+})_2$ have been investigated to provide mechanistic insight into sulfoxidation by $[(L)Mn^{IV}(O)]^{2+}–(Sc^{3+})_2$. In chapter 5, diprotonated nonheme manganese(IV)-oxo complexes, $[(L)Mn^{IV}(O)]^{2+}–(HOTf)_2$, were synthesized by adding HOTf (trifluoromethanesulfonic acid) to $[(L)Mn^{IV}(O)]^{2+}$ complexes and were characterized by various spectroscopic methods. The fundamental electron-transfer properties of $[(L)Mn^{IV}(O)]^{2+}–(HOTf)_2$ have also been investigated to compare the reactivities with OAT and HAT reactions. Such contrasting effects by binding of metal ions and protons observed in OAT and HAT reactions provides valuable insights into fine control of the reactivity of metal-oxo complexes, which is certianly requried to develop efficient catalytic oxidation sytems including water oxidation.