Sequential Oxidation Pathways Initiated by a Bis(μ-oxo)dinickel(III) Complex in Aliphatic C-H Bond Functionalization

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Aliphatic C-H bond functionalization by various metal–active oxygen species M_m/O_n such as superoxo, peroxo, high-valent bis(μ-oxo)dimetal complexes, etc. is of great interest for understanding the reaction mechanisms of metalloenzymes and utilizing metal complexes as oxidation catalysts. A variety of synthetic high-valent bis(μ-oxo)dimetal complexes (M = Fe, Co, Ni, and Cu) has been developed and provided chemical basis for understanding of structural and spectroscopic properties, and reactivities of the high-valent bis(μ-oxo)dimetal complexes.

Reaction of $[Ni_2(\mu\text{-}OH)_2(Me_2\text{-}tpa)_2]^{2+}$ (**1**) with H_2O_2 causes oxidation of one of the methyl groups of a supporting ligand to produce carboxylate and alkoxide ligands as final oxidation products, where Me_2-tpa = bis(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine. A series of the sequential reaction intermediates, bis(μ-oxo)dinickel(III) $[Ni_2(\mu\text{-}O)_2(Me_2\text{-}tpa)_2]^{2+}$ (**2**), bis(μ-superoxo)dinickel(II) $[Ni_2(\mu\text{-}O_2)_2(Me_2\text{-}tpa)_2]^{2+}$ (**3**), (μ-hydroxo)(μ-alkylperoxo)dinickel(II) $[Ni_2(\mu\text{-}OH)(\mu\text{-}OOCH_2\text{-}Me\text{-}tpa)(Me_2\text{-}tpa)]^{2+}$ (**4**), and bis(μ-alkylperoxo)dinickel(II) $[Ni_2(\mu\text{-}OOCH_2\text{-}Me\text{-}tpa)_2]^{2+}$ (**5**) complexes produced in the oxidation pathways was successfully characterized by various physicochemical measurements including X-ray crystallography and their oxidation pathways were investigated.