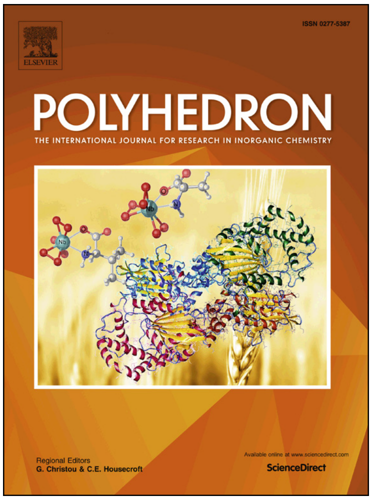

Catalysis of Alkene Epoxidation by Manganese (II) and (III) Complexes of both Schiff base and Reduced Schiff base Ligands utilizing Environmentally Benign H_2O_2

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Abstract:

Mono and disubstituted tridentate Schiff base ligands were synthesized from the reaction of 2(2-aminoethyl)pyridine with 5-bromosalicylaldehyde ($H\text{-}L^1$) and 3, 5-dibromosalicylaldehyde ($H\text{-}L^2$) respectively, which were subsequently reacted with $NaBH_4$ to yield the corresponding reduced Schiff base ligands $H\text{-}rL^1$ and $H\text{-}rL^2$. The complexes; $Mn^{III}\text{-}(L^1)_2$ (1), $Mn^{III}\text{-}(rL^1)_2$ (3), and $Mn^{II}\text{-}(L^2)_2$ (2), $Mn^{II}\text{-}(rL^2)_2$ (4) were obtained by the reaction of the ligands with $\{Mn(ClO_4)_2.6H_2O\}$. The ligands and complexes were characterized by UV-Visible, ESI-MS and FT-IR spectroscopy. The ^1H NMR spectra of the ligands as well as the crystal structures, and electrochemical properties of the complexes were obtained. The crystal structures of $Mn^{III}\text{-}(L^1)_2$ and $Mn^{II}\text{-}(L^2)_2$ show coordination of the ligands in tridentate mode in octahedral geometry. Cyclic voltammetric studies of $Mn\text{-}(L^1)_2$ and $Mn\text{-}(L^2)_2$ in acetonitrile solution show two prominent reversible peaks attributed to the redox processes: Mn(II)/Mn(III), (E½ = 0.203 - (-0.204 V) and Mn(III)/Mn(IV), (E½ = 1.103 - 0.195 V) vs. Ag/AgCl while that of $Mn\text{-}(rL^4)_2$ showed three quasi reversible peaks suggesting three redox couples: Mn(II)/Mn(III) ($E_{1/2}$ = -0.109); Mn(III)/Mn(IV), ($E_{1/2}$ = 0.125 and (Mn(IV)/Mn(V), ($E_{1/2}$ = 0.649) vs Ag/AgCl. Epoxidation of cyclohexene and 1-hexene by hydrogen peroxide catalyzed by the manganese complexes gave epoxide yield of 42-53% with a turnover of 10.50-13.25 after 20 hours of reaction for the reduced Schiff base complexes $\{Mn^{III}\text{-}(rL^1)_2$ and $Mn^{II}\text{-}(rL^2)_2\}$ at 0°C.

Keywords: Schiff base, Reduced Schiff base, Manganese complexes, Co-catalysts, Epoxidation, Catalysis

1. Introduction