



Dioxidomolybdenum(VI) complexes chelated with N⁴-(3-methoxyphenyl)thiosemicarbazone as molybdenum(IV) precursors in oxygen atom transfer process and oxidation of styrene

T.M. Asha^a, M. Sithambaresan^b, M.R. Prathapachandra Kurup^{a,c,*}

^a Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India

^b Department of Chemistry, Faculty of Science, Eastern University, Chenkalady, Sri Lanka

^c Department of Chemistry, School of Physical Sciences, Central University of Kerala, Tejaswini Hills, Periyar, Kasaragod 671 316, Kerala, India

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ABSTRACT

Four new mononuclear dioxidomolybdenum(VI) complexes of the type [MoO₂LD] (where D = methanol (1), ethanol (2), propanol (3) and [MoO₂LD]₂-D (where D = 4-picoline (4)) have been synthesized by the reaction of [MoO₂(acac)₂] with the thiosemicarbazone (H₂L) derived from 3-ethoxy-2-hydroxybenzaldehyde and N⁴-(3-methoxyphenyl)thiosemicarbazone in presence of donor solvents like methanol, ethanol, propanol and 4-picoline. Crystal and molecular structures of the complexes were determined by single crystal X-ray diffraction analysis. All the complexes portrayed similar mononuclear structures where the thiosemicarbazone is bonded to molybdenum(VI) ion as a bidentate tridentate agent. The molybdenum(VI) centre in complexes 1–4 is six coordinate by the thiosemicarbazone, two oxido groups and an oxygen or nitrogen atom from the donor solvent molecules. The complexes 1–4 exhibit oxygen atom transfer to PPh₃ in acetonitrile medium in presence of N–N bidentate donors to form complexes of the form [Mo^(IV)OL(N–N)] (where N–N = 2,2'-bipyridine (5) or 1,10-phenanthroline (6)). The complexes were further characterized by elemental analysis, spectroscopic methods (IR, UV–Vis and ¹H NMR) and thermogravimetric analysis. The electrochemical behaviour of these complexes have been investigated for an insight into the redox behaviour of the molybdenum(VI) centres in these complexes. Hirshfeld surface analysis was successfully employed for exploring the coordination geometries and various non-covalent interactions present in their crystal structures. Furthermore, the catalytic abilities of 1–4 were tested for the oxidation of styrene using aqueous H₂O₂ as oxidant and NaHCO₃ as co-catalyst. The reaction condition for all-out catalytic proficiency of the catalysts 1–4 were examined by studying the effect of various parameters such as the amount of catalyst, H₂O₂, co-catalyst (NaHCO₃) and solvent (CH₃CN) as well as temperature of the reaction. Almost 97–98% product selectivity was attained for the oxidation of styrene to styrene oxide.

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1. Introduction

Catalytic olefin epoxidation in liquid-phase serve as an outstanding topic in organic synthesis [1–3]. The epoxy compounds so formed can be used as such [4–7] or find application in the synthesis of a wide range of other commodity chemicals [8]. Hydrogen peroxide, among the various oxidants available, serves as the best terminal oxidant next to dioxygen from environmental as well as economic considerations [8,9]. Hence an unlimited deal of work has been done on the homogenous catalytic epoxidation by making

use of hydrogen peroxide as oxidant [10,11]. Likewise, among the various transition metals used as catalysts [1–3,12–14], high-valent dioxidomolybdenum(VI) complexes containing the *cis*-[MoO₂]²⁺ core have been successfully studied in recent years due to their biological relevance to molybdenum oxotransferase [15] as well as their catalytic properties towards oxygen atom transfer (OAT) reactions [16–18].

Moreover, the influence of various co-ligand, LL' on the steric as well as redox properties of the complexes of the type [MoO₂LD], have been largely explored [19–22]. Among them, O, S based systems *viz.*, thiosemicarbazones have received considerable attention owing to the essential role played by these atoms in the coordination sphere of molybdenum containing enzymes [15,23–25]. Oxo-peroxo molybdenum complexes catalyse oxidation of a

* Corresponding author at: Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India.

E-mail address: mrp@cukerala.ac.in (M.R. Prathapachandra Kurup).