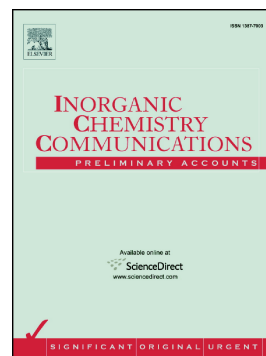


Accepted Manuscript

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PII: S1387-7003(17)30525-7
DOI: doi: [10.1016/j.inoche.2017.07.025](https://doi.org/10.1016/j.inoche.2017.07.025)
Reference: INOCHE 6722

To appear in: *Inorganic Chemistry Communications*

Received date: 19 June 2017

Revised date: 15 July 2017

Accepted date: 18 July 2017

Please cite this article as: Mojtaba Bagherzadeh, Saeed Ataie, Hamed Mahmoudi, Jan Janczak, Synthesis, structure characterization and study of a new molybdenum Schiff base complex as an epoxidation catalyst with very high turnover numbers, *Inorganic Chemistry Communications* (2017), doi: [10.1016/j.inoche.2017.07.025](https://doi.org/10.1016/j.inoche.2017.07.025)

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Synthesis, Structure Characterization and Study of a New Molybdenum Schiff Base Complex as an Epoxidation Catalyst with Very High Turnover Numbers

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Abstract: The reaction between $[\text{MoO}_2(\text{acac})_2]$ and an ONO type Schiff-base ligand (L= 4-bromo-2-((2-hydroxy-5-methylphenylimino)methyl)phenol)) resulted a new oligomer molybdenum complex ($[\text{MoO}_2(\text{L})_n]$). The oligomer complex was characterized by elemental analysis, FT-IR, ^1H and ^{13}C NMR spectroscopies. A suitable single crystal of the complex was grown in DMSO and characterized by X-ray single crystal diffraction as monomer stabilized by one DMSO molecule, $[\text{MoO}_2\text{L}(\text{DMSO})]$. The $[\text{MoO}_2(\text{L})_n]$ complex was used as a catalyst in epoxidation of olefins. Besides the high activity and selectivity, very high turnover numbers were a remarkable advantage of the catalytic system.

Keywords: Mo(VI) complex, Schiff base ligand, Olefin epoxidation, Oligomer complex, Crystal structure

During recent decades, epoxidation of alkenes has attracted certain attention, due to the useful products such as epoxy resins, perfumes, cosmetics, pharmaceuticals and polymers in different areas like industry and medicine [1-5]. Molybdenum complexes, as an epoxidation catalyst, play a great role [6-9]. The presence of an active site of $\text{Mo}=\text{O}$ grants this catalytic activity to molybdenum complexes, like molybdenum enzymes [10,11]. Also, employing non-toxic procedures and materials having friendly treatment with the environment is very important [12]. The nature of ligands directly affect the catalytic activity and selectivity [13] and Schiff-bases can be referred as one of the efficient ligands [14-16]. In this study, a new oligomer molybdenum complex has been synthesized [17], (Fig. 1.), through the reaction of $[\text{MoO}_2(\text{acac})_2]$ [18] and Schiff-base ligand (4-bromo-2-((2-hydroxy-5-methylphenylimino)methyl)phenol) [19].

The oligomer complex was rearranged to monomer structure in DMSO solution in the suitable crystalline form stabilized by one DMSO molecule and characterized by X-ray crystallography. The oligomer complex was utilized as a homogeneous catalyst in the epoxidation of olefins. The presence of a band at 3031 cm^{-1} (OH) in the ligand IR spectrum [19] and disappearance of this band in the complex spectrum, and also a shift in $\nu(\text{N}=\text{C})$ band from 1627 cm^{-1} to 1610 cm^{-1} suggests the ligand coordination to the metal through the oxygen and nitrogen atoms. The oligomer complex IR spectrum shows one band at 925 cm^{-1} related to $\text{Mo}=\text{O}$ group and one band in 807 cm^{-1} belonged to $\text{Mo}-\text{O}-\text{Mo}$ [20]. On the other hand, the IR spectrum belonged to an orange crystal of monomer complex indicates two close bands in 898 and 918 cm^{-1} related to two $\text{Mo}=\text{O}$ groups [20]. Two singlet peaks (^1H , OH) at 13.89 and 9.55 ppm in ligand ^1H NMR spectrum indicate two phenolic protons [19], and they are disappeared in the complex spectrum. As well as, the shift of singlet (^1H , $\text{N}=\text{CH}$) from 8.96 to 9.21 ppm proves that the complexation happens through the

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