



Synthesis, crystal structure and DFT studies of a new dioxomolybdenum (VI) Schiff base complex as an olefin epoxidation catalyst



Zeinab Asgharpour^a, Faezeh Farzaneh^{a,*}, Alireza Abbasi^b, Mina Ghiasi^a

^a Department of Chemistry, Faculty of Physics & Chemistry, Alzahra University, P.O. Box 1993891176, Vanak, Tehran, Iran

^b School of Chemistry, College of Science, University of Tehran, P.O. Box 14155 6455, Tehran, Iran

ARTICLE INFO

Article history:

Received 8 July 2015

Accepted 5 September 2015

Available online 21 September 2015

Keywords:

Mo complex
Schiff base ligand
Epoxidation
Alkenes
DFT studies

ABSTRACT

A cis-dioxomolybdenum(VI) complex was prepared from Mo(acac)₂ and a Schiff base ligand derived from 2-hydroxy-1-naphthaldehyde (Naph) and L-histidine (His) in ethanol and was designated as MoO₂(Naph-His). Characterization of MoO₂(Naph-His) was carried out by means of elemental analysis, ¹H NMR, ¹³C NMR, FT-IR, UV-Vis and TGA techniques. The crystal structure of MoO₂(Naph-His), determined by single-crystal X-ray crystallography, revealed that the coordination of Mo in the complex is a distorted octahedron, formed by a tetradentate Naph-His Schiff base ligand and two binding oxygen atoms. The optimized geometrical parameters obtained by DFT calculations are in good agreement with the single XRD data. It was found that MoO₂(Naph-His) successfully catalyzes the epoxidation of cyclooctene, cyclohexene and norbornene with 80–100% conversions and 54–100% selectivities. Based on the obtained results, the heterogeneity and reusability of the catalyst seems promising.

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1. Introduction

The enzymatic role of molybdenum compounds in biological reactions has created a tremendous impetus in the synthesis of a number of model complexes mimicking oxotransferase molybdoenzymes [1–4]. In this regard, many stable molybdenum complexes with oxygen-, nitrogen- and sulfur-containing ligands have been prepared. Molybdenum(VI) Schiff base complexes with a cis-MoO₂ core are excellent enzyme model systems for the active sites of molybdo-enzymes, such as xanthine oxidase, nitrogenase and sulfite oxidase. Possessing an Mo=O unit, they have widely been used as catalysts in industrial processes, such as epoxidation, sulfoxidation and hydroxylation of olefins [5–9].

Coordination complexes of Mo with Schiff base ligands have wide applications in electrochemistry [10] and biological modelling [11], as antioxidant [12] and antibacterial agents [13], and as catalysts for hydrogen generation [14], alkene epoxidations [15,16] and sulfide oxidations [17]. In order to mimic biological systems, a number of dioxomolybdenum complexes have been synthesized and characterized [18–22]. The activity of these

complexes varies with the ligand type and coordination sites. In spite of the synthesis of many Mo complex Schiff bases, there are few reports on the preparation of Schiff bases with amino acids [23,24]. Amino acids are efficient biologically active and cytotoxic agents and are considered as anticancer and antibacterial reagents [25,26]. Amino acid Schiff bases are sensitive to moisture and decompose when exposed to air. Therefore, they are usually generated immediately prior to use for complexation. It is particularly significant that isolated crystalline amino acid Schiff bases have rarely been reported [27].

The catalytic epoxidation of alkenes is a reaction of great industrial interest because epoxides are widely used as intermediate chemicals for making valuable products, such as chiral pharmaceuticals, epoxy resins, epoxy paints, surfactants, pesticides, agrochemicals, perfume materials and sweeteners. Epoxides have also been numerously applied as precursors in the production of fine chemicals [28–34]. The type of ligand structure present in the complex and the catalytic reaction conditions have a significant effect on the catalytic activity of complexes involving the Mo(VI) metal center [35]. As a result, several research groups have focused on the design of new Mo(VI) complexes and their potential applications.

In this study, an attempt has been made to prepare a new Schiff base complex of Mo with His and Naph and using it as a catalyst for the epoxidation of some alkenes.

* Corresponding author. Tel.: +98 21 88258977; fax: +98 21 88041344.

E-mail addresses: faezeh_farzaneh@yahoo.com, Farzaneh@alzahra.ac.ir (F. Farzaneh).

2. Experimental

2.1. Materials and characterization

All materials were of commercial reagent grade and used without further purification. *t*-Butyl hydroperoxide (TBHP) was purchased from Fluka, 2-hydroxy-1-naphthaldehyde (Naph), *L*-histidine (His), sodium acetate, hydrogen peroxide (30%), cyclooctene, diethyl ether and ethanol were purchased from Merck Chemical Company. FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer using KBr pellets over the range 4000–400 cm⁻¹. The UV-Vis measurements were performed on a double beam UV-Vis Perkin Elmer Lambda 35 spectrophotometer. Single crystal measurement was performed on an Agilent Super Nova Dual single crystal diffractometer. Intensity data were collected using graphite monochromatised Mo K α radiation ($k = 0.71073 \text{ \AA}$). Chemical analyses of samples were determined with a Perkin Elmer atomic absorption spectrometer (AAS). TGA thermal curve measurement was carried out with a Perkin Elmer Pyris 1. Oxidation products were analyzed by GC and GC-MS using an Agilent 6890 Series with an FID detector, HP-5, 5% phenyl-methyl siloxane capillary and an Agilent 5973 Network, mass selective detector, HP-5 MS 6989 Network GC system.

2.2. Preparation of [MoO₂(Naph-His)]

Initially, Naph (0.172 g, 1 mmol) was dissolved in ethanol (2 mL). This solution was then added to a solution of His (0.155 g, 1 mmol in 2 mL water). Upon addition of an aqueous sodium acetate solution (0.164 g, 2 mmol in 1 mL water), the color changed to yellow. To this solution was added MoO₂(acac)₂ (0.278 g, 0.85 mmol in 2 mL ethanol, prepared according to the literature method [18]), followed by heating at reflux for 3 h. The yellow resultant solid was then filtered, washed with water, ethanol and diethyl ether, and then dried in air at room temperature. X-ray crystals of the complex [MoO₂(Naph-His)] were obtained by slow diffusion of diethyl ether into a saturated [MoO₂(Naph-His)] solution in CH₃CN/EtOH/CHCl₃ (1:1:0.5).

Yield: 50%. Decomposition point: 297 °C. Anal. Calc. for C₁₇H₁₃-MoN₃O₅ ($M = 435.24 \text{ g mol}^{-1}$): Mo, 22.04; C, 46.91; H, 3.01; N, 9.65. Found: Mo, 21.98; C, 46.90; H, 2.99; N, 9.63%. FT-IR (KBr pellet) cm⁻¹: 1625 (C=N), 1557, 1386 (COO), 1557 (C=C), 547 (Mo-O), 497 (Mo-N), 910, 920 (cis-MoO₂) [36,20]. UV-Vis (methanol) λ_{max} (nm): 270, 285, 346, 414 [21]. ¹H NMR (DMSO-d₆) δ , ppm: 3.19–3.24 (m) (b-CH), 7.11 (m) (imidazole-5-H), 7.56–7.69 (m) (Ar-H), 8.37 (d) (imidazole-2-H), 9.00 (s) (CH=N), 12.82 (brs) (imidazole N-H). ¹³C NMR (DMSO-d₆) δ , ppm: 116.0 (imidazole-C), 118.8 (Ar), 122.7 (Ar), 123.0 (Ar), 133.1 (A), 135.1 (imidazole-C), 136.8 (Ar), 162.5 (CH=N), 165.4 (Ar), 174.6 (C=O) [36].

2.3. General procedure for the oxidation of alkenes

All oxidation reactions of alkenes (norbornene, cyclohexene and cyclooctene) were carried out in a round bottom flask equipped with a magnetic stirrer and a water-cooled condenser. Typically, [MoO₂(Naph-His)] as catalyst (0.025 g) in CCl₄ (5 mL) and alkene (10 mmol) with TBHP (14 mmol) were mixed and the mixture was heated at reflux for 8 h. After separation of the catalyst, the filtrate was subjected to GC and GC-Mass for analyses.

2.4. X-ray crystallography

Crystallographic data were collected on a MAR345 dtb diffractometer equipped with image plate detector using Mo K α radiation (0.71073 Å). The structure was solved by direct methods using

Table 1

Selected crystallographic data for the [MoO₂(Naph-His)] complex.

Empirical formula	C ₁₇ H ₁₃ MoN ₃ O ₅
Formula weight	434.24
<i>T</i> (K)	293(2)
λ (Å)	0.71073
Crystal system	orthorhombic
Space group	<i>P</i> 2(1)2(1)2
<i>a</i> (Å)	7.6421(15)
<i>b</i> (Å)	15.405(3)
<i>c</i> (Å)	13.828(3)
<i>V</i> (Å ³)	1627.9(6)
<i>Z</i>	4
μ (mm ⁻¹)	0.842
<i>D_x</i> (Mg m ⁻³)	1.776
<i>R_{int}</i>	0.0422
θ (°)	1.98–26.00
Index ranges	−9 ≤ <i>h</i> ≤ 9 −19 ≤ <i>k</i> ≤ 18 −16 ≤ <i>l</i> ≤ 17
Reflections collected	9752
Independent reflections	3205
Independent reflections [<i>I</i> > 2 σ (<i>I</i>)]	3046
Data/restraints/parameters	3205/0/205
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0366 <i>wR</i> ₂ = 0.0754
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0416 <i>wR</i> ₂ = 0.0778

Table 2

Selected experimental (Exp.) and calculated (B3LYP/3-21G and B3LYP/6-31g*) bond lengths (Å) and angles (°) for [MoO₂(Naph-His)].

Connected atom	Exp.	B3LYP/3-21G	B3LYP/6-31g*
<i>Bond distance</i> (Å)			
Mo–O ₅	1.696	1.739	1.70
Mo–O ₄	1.696	1.728	1.71
Mo–O ₃	1.941	1.999	2.00
Mo–O ₁	2.048	2.005	2.00
Mo–N ₁	2.205	2.261	2.21
Mo–N ₂	2.357	2.432	2.32
Standard deviation		0.12	0.085
<i>Bond angle</i> (°)			
O ₅ –Mo–O ₄	105.70	106.08	106.00
O ₅ –Mo–O ₃	103.63	98.83	100.20
O ₄ –Mo–O ₃	96.48	96.14	96.50
O ₅ –Mo–O ₁	98.85	102.99	100
O ₄ –Mo–O ₁	94.02	96.40	95.12
O ₅ –Mo–N ₁	158.02	153.29	155.20
O ₄ –Mo–N ₁	95.41	100.61	98.30
Standard deviation		9.77	5.56
<i>Dihedral angle</i> (°)			
O ₄ –Mo–O ₁ –C ₁	116.2	117.7	117.0
O ₅ –Mo–O ₁ –C ₁	−137.3	−134.64	−135.5
N ₁ –Mo–O ₁ –C ₁	21.7	17.93	20.12
N ₂ –Mo–O ₁ –C ₁	−56.2	−57.53	−55.3

SHELXS-97 and refined using the full-matrix least-squares method on *F*², SHELXL-97 [37]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at ideal positions and refined using a riding model. Crystallographic data, details of collected data and structure refinement are listed in Table 1. Selected bond lengths and angles are shown in Table 2.

2.5. Computational details

All calculations were carried out with the Gaussian program series 2003 [38]. The optimization of the geometry was performed employing a hybrid Hartree-Fock-density functional scheme, the adiabatic connection method-Becke three-parameter with Lee-Yang-Parr (B3LYP) [39] density functional theory (DFT) [40] with

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