



## Dioxomolybdenum(VI) complexes with naphtholate-oxazoline ligands in catalytic epoxidation of olefins



Pedro Traar, Jörg A. Schachner, Bernhard Stanje, Ferdinand Belaj, Nadia C. Mösch-Zanetti\*

Institute of Chemistry, Karl–Franzens–University Graz, Stremayrgasse 16, Graz 8010, Austria

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### ABSTRACT

Synthesis, characterization and catalytic epoxidation experiments of two new dioxomolybdenum(VI) complexes  $[\text{MoO}_2(\text{L})_2]$  (**3a–b**) equipped with *O,N*-bidentate naphtholate-oxazoline ligands  $\text{L} = \mathbf{2a–b}$  are described. Ligands **2a–b** (**2a** = 2-(4,5-dihydrooxazol-2-yl)naphthalen-1-ol, **2b** = 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)naphthalen-1-ol) were obtained via a two-step synthesis starting from 1-hydroxy-naphthoic acid. Complexes **3a–b** were synthesized starting from  $[\text{MoO}_2(\text{acac})_2]$  and obtained in good yields as air and moisture stable solids. The molecular structure of both complexes **3a–b** were determined by single crystal X-ray diffraction analysis, showing the expected octahedral coordination of the Mo center by two bidentate ligands of **2a** or **2b** and two terminal oxo ligands. Interestingly, for complex **3b** two different coordination isomers with regards to the orientation of the bidentate ligands (*N,N-trans* **3b** and *N,N-cis* **3b'**), were obtained in the solid state. Both complexes **3a–b** show high catalytic activities and selectivities in the epoxidation of various terminal and internal olefins at low catalyst loadings of 0.05 mol% with *tert*-butylhydroperoxide. With cyclooctene TON of 5000 could be reached, for styrene selectivities of >90% were achieved.

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### 1. Introduction

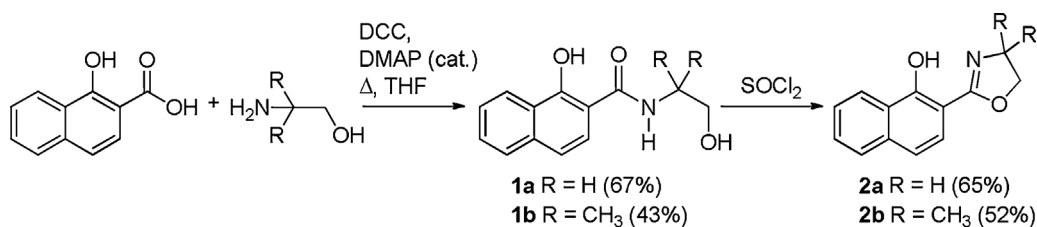
The propensity of oxomolybdenum species to perform oxygen atom transfer (OAT) reactions has been observed in the realm of biology and has been exploited in industrial chemistry. Several Mo containing enzymes are known that take part in various metabolic OAT reactions in the living cell [1–3]. The mechanism of these molybdoenzymes is still under investigation; therefore several research groups including us have been studying synthetic, functional or structural analogous molybdenum complexes to further elucidate mechanistical details [4–12]. OAT reactions on an industrial scale include the epoxidation of olefins. Epoxides are very important intermediates in the chemical industry, in particular for the synthesis of various polymers (polyglycols, polyamides, polyurethanes etc.) [13]. Production of propylene oxide makes up for the biggest share on the market, with a global capacity of eight million tons per year [14]. In order to avoid the non-economical use of stoichiometric amounts of oxidants like peracids, NaOCl or iodosobenzene, many different transition metal catalysts, also containing molybdenum, have been

developed [14–16]. One of the industrially used heterogeneous epoxidation catalyst is formed by the reaction  $[\text{Mo}(\text{CO})_6]$  and alkylhydroperoxides, and many homogeneous molybdenum catalysts have been investigated in order to improve this important reaction [17–22]. Phenolate–oxazoline ligands were amongst the first reported examples of active molybdenum(VI) epoxidation catalysts and have been further investigated since [19,23–26].

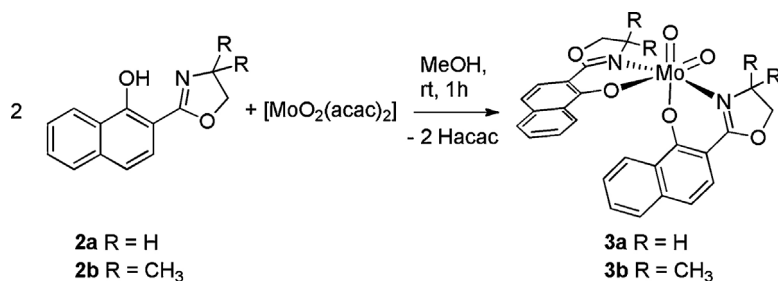
We have an ongoing interest in the chemistry of dioxomolybdenum(VI) and oxorhenium(V) complexes using different *O,N*-bidentate ligands. With a phenolate–pyrazole ligand we obtained very active molybdenum and rhenium epoxidation catalysts for a range of substrates [27,28]. Employing *O,N*-Schiff base ligands in dioxomolybdenum(VI) complexes we could selectively epoxidize the challenging substrate styrene [29]. Also dimeric Mo(V) complexes equipped with Schiff base ligands are active epoxidation catalysts [30]. We are furthermore interested in mechanistic aspects of OAT reactions relevant to metalloenzymes [31–33]. Therefore, we would like to report on the synthesis and characterization of two new entries into the family of aryloxide–oxazoline ligands, namely naphtholate–oxazoline ligands **2a–b** and the dioxomolybdenum(VI) complexes **3a–b** thereof. Furthermore, complexes **3a–b** were tested as potential catalysts in the epoxidation of various challenging olefins. Thereby the influence of the aromatic moiety of the *O,N*-bidentate ligand can be

\* Corresponding author. Tel.: +433163805286.

E-mail address: [nadia.moesch@uni-graz.at](mailto:nadia.moesch@uni-graz.at) (N.C. Mösch-Zanetti).



**Scheme 1.** Synthesis of benzamides **1a-b** and oxazoline ligands **2a-b** (isolated yields in brackets).



**Scheme 2.** Synthesis of complexes **3a** and **3b**.

studied and compared to the published phenolate–oxazoline complexes.

## 2. Results and discussion

Ligands **2a-b** were synthesized via a modified two step reaction in analogy to published procedures [34,35]. There, the authors started from 1-methoxynaphthalene in order to obtain 2-(1-methoxynaphthalen-2-yl)-4,4-dimethyl-4,5-dihydrooxazole, which represents the methyl ether of ligand **2b** [34,35]. In order to obtain the free naphtholate–oxazoline ligands we started from commercially available 1-hydroxy-2-naphthoic acid and the respective aminoalcohol and synthesized the benzamides **1a-b** via a Steglich condensation in refluxing tetrahydrofuran (THF) (Scheme 1). Optimal conditions for the condensation reaction of **1a-b** were found using dicyclohexylcarbodiimide (DCC), 1-hydroxy-2-naphthoic acid and the respective aminoalcohol in the ratio of 1/1.5/1.1 molar equivalents in the presence of a catalytic amount of dimethylaminopyridine (5 mol%, DMAP). Amides **1a-b** can be isolated and purified by column chromatography or used directly in a one pot synthesis for the next step (see Supporting Information). The cyclization to obtain the respective oxazoline ligands **2a-b** was achieved in analogy to a published procedure with thionyl chloride [36]. Compounds **2a-b** represent bidentate *O,N*-coordinating ligands, where the hydroxyl group is easily deprotonated by bases like  $\text{NEt}_3$ , whereby they become mono-anionic (Scheme 2).

Dioxomolybdenum(VI) complexes **3a-b** were obtained by stirring a mixture of  $[\text{MoO}_2(\text{acac})_2]$  and two equivalents of the corresponding ligand **2a** or **2b** in methanol for 1 h [23]. The so obtained precipitates were filtered and washed with small amounts of MeOH to give **3a-b** in analytically pure form as orange–yellowish solids (yield: **3a** 78%; **3b** 63%).

Both complexes are barely soluble in polar solvents like methanol, chloroform or dichloroethane. For this reason  $^1\text{H}$  NMR spectra of **3a-b** had to be measured in deuterated methanol at  $50^\circ\text{C}$ . Because of their low solubility we were unable to obtain meaningful  $^{13}\text{C}$  NMR spectra. Due to the bidentate nature of ligands **2a-b** a total of three geometrical isomers are possible for disubstituted *cis*-dioxomolybdenum(VI) complexes, depending on the coordinating atoms in *trans* position to the terminal oxo groups: both N-donors *trans* to the terminal oxo ligands (N,N-isomer), both naphthoxy groups *trans* to the terminal oxo ligands (O,O-isomer) or

**Table 1**

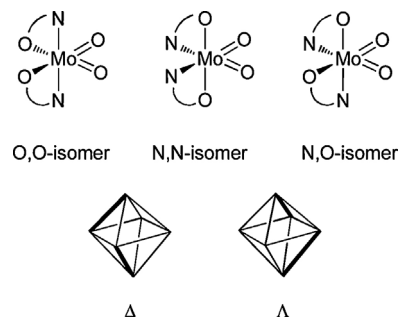
Selected IR bond stretching frequencies of ligands **2a-b** and complexes **3a-b**.

	Bond stretching frequencies, $\nu$ ( $\text{cm}^{-1}$ )			
	<b>2a</b>	<b>2b</b>	<b>3a</b>	<b>3b</b>
$\nu_{\text{C=N}}$	1626	1620	1572	1573
$\nu_{\text{Mo=O}}$	–	–	878, 866	885, 867

one N-donor and one naphthoxy group *trans* to the terminal oxo ligands (N,O-isomer). The asymmetric coordination of the bidentate ligands **2a-b** creates a chiral environment around the Mo atom, so that each of the three possible isomers forms a pair of diastereomers  $\Delta$  and  $\Lambda$  [23]. The occurrence of only one set of ligand resonances in the proton spectrum of **3a-b** evidences the formation of a  $\text{C}_2$ -symmetric isomer, either the N,N-isomer or O,O-isomer (Fig. 1).

The formation of complexes **3a-b** was also apparent by IR spectroscopy (Table 1). Upon coordination of the respective ligand **2a-b** a shift to lower wave numbers of the  $\nu_{\text{C=N}}$  vibration is observed as well as the appearance of two diagnostic  $\nu_{\text{Mo=O}}$  vibrations between 850 and  $950\text{ cm}^{-1}$  [23,25,37–39]. Mass spectrometry as well as elemental analysis are also consistent with the formula of dioxomolybdenum(VI) complexes **3a-b**.

Single crystals of **3a-b** were obtained from concentrated solutions of methanol. The  $\text{C}_2$ -symmetric structures were confirmed by single crystal X-ray diffraction analysis for both complex **3a-b**. Complex **3a** displayed the O,O-isomer in the solid state (vide infra). For compound **3b** single crystals of two different colors were obtained, with a majority of orange crystals and a small amount of



**Fig. 1.** Possible geometrical and optical isomers of complexes **3a-b**.

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