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

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ABSTRACT

Synthesis, characterization and catalytic epoxidation experiments of two new dioxomolybdenum(VI) complexes $[MoO_2(L)_2]$ (**3a-b**) equipped with *O,N*-bidentate naphtholate-oxazoline ligands L = **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 $[MoO_2(acac)_2]$ 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.

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 $[Mo(CO)_6]$ 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

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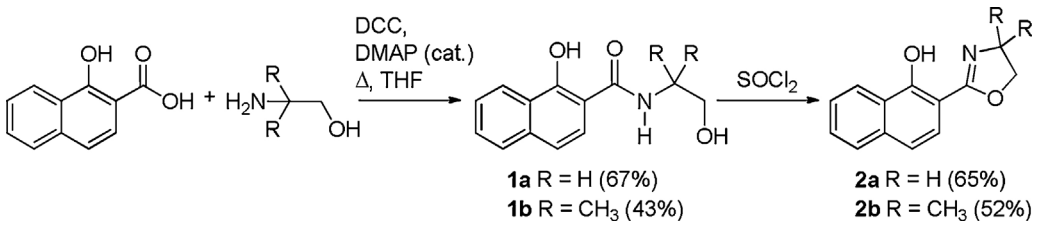
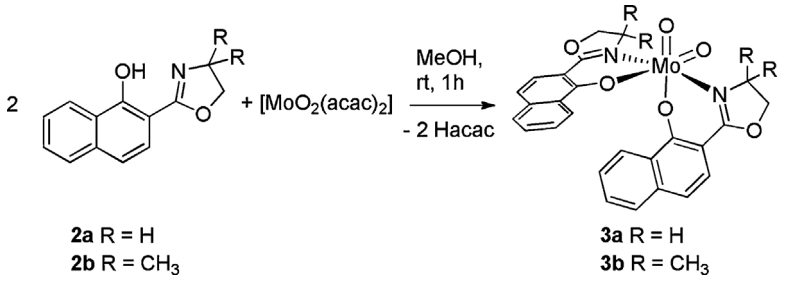


Scheme 1. Synthesis of benzamides **1a-b** and oxazoline ligands **2a-b** (isolated yields in brackets).



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 dicyclohexylcarbodiimid (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 NEt_3, whereby they become mono-anionic (Scheme 2).

Dioxomolybdenum(VI) complexes **3a-b** were obtained by stirring a mixture of $[MoO_2(acac)_2]$ 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 ^1H NMR spectra of **3a-b** had to be measured in deuterated methanol at 50 °C. Because of their low solubility we were unable to obtain meaningful ^{13}C NMR spectra. Due to the bidentate nature of ligands **2a-b** a total of three geometric 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 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 Δ and Λ [23]. The occurrence of only one set of ligand resonances in the proton spectrum of **3a-b** evidences the formation of a C_2-symmetric isomer, either the N,N-isomer or O,O-isomer (Fig. 1).

Table 1
Selected IR bond stretching frequencies of ligands **2a-b** and complexes **3a-b**.

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

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 $\nu_{C=N}$ vibration is observed as well as the appearance of two diagnostic $\nu_{Mo=O}$ vibrations between 850 and 950 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 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

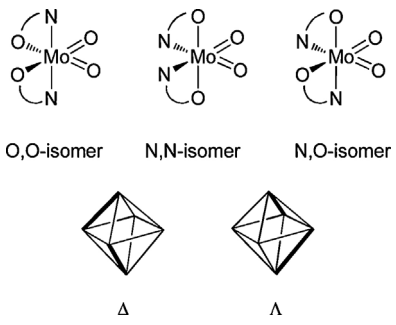


Fig. 1. Possible geometrical and optical isomers of complexes **3a-b**.

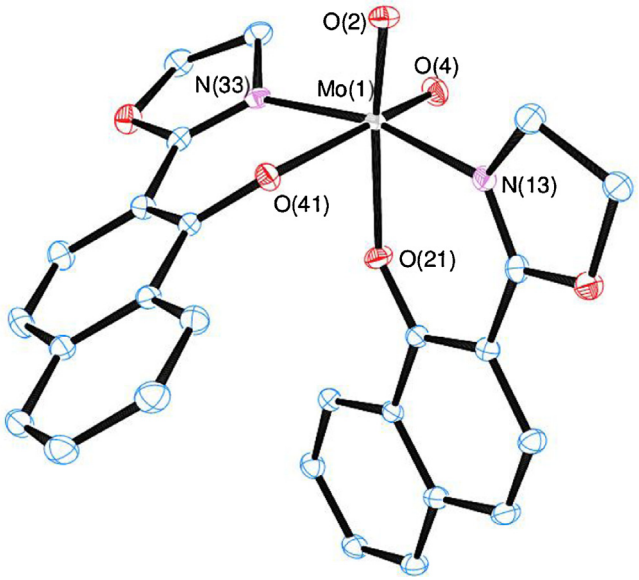


Fig. 2. Molecular structures of **3a** showing the atomic numbering scheme. Probability ellipsoids are drawn at the 50% level; H atoms are omitted for clarity.

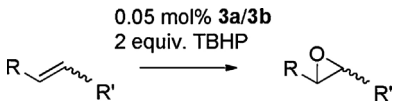
yellow plates. The crystals could be separated under the microscope and analyzed individually. The major orange crystalline fraction thereby displayed the O,O-isomer, which is the same isomer as in **3a**, whereas the yellow crystals displayed the N,N-isomer (**3b'**). Since **3b'** only formed in traces, we were not able to isolate a significant amount of **3b'** in order to obtain full analytical and experimental data on **3b'.** Therefore all the epoxidation experiments were done with complex **3b**. In the ^{1}H NMR spectrum of **3b** no signals for **3b'** could be detected. This is possible due to the general low solubility of the complexes. However, isomerisation in solution might be occurring, but again the low solubility prevented further investigations by e.g. VT-NMR spectroscopy.

The crystal structure analysis of **3a** confirmed the formation of *cis*-dioxomolybdenum(VI) complex with the two oxazoline N atoms N(13) and N(33) *trans* to each other and the two naphtholate oxygen atoms O(21) and O(41) *trans* to two terminal oxo ligands O(2) and O(4) (O,O-isomer) (Fig. 2).

All bond lengths and angles in **3a** fall within the expected range for an octahedral dioxomolybdenum(VI) complex (Table 2) [23,25,28,37]. The distorted octahedral coordination is most likely a result of the small bite angle of bidentate ligand **2a**, which is reflected for example by the smaller than 90° angle of O(41)-Mo(1)-N(33) of 78.96(5)°. For complex **3b** single >crystals of both the O,O-isomer (**3b**) as well as the N,N-isomer (**3b'**) could be obtained and characterized by X-ray crystallography. The asymmetric unit cell of **3b** consists of two half molecules, each one arranged around two-fold rotation axes parallel to the monoclinic b axis through the Mo atoms (for full details see SI). Also for **3b'**, the asymmetric unit cell contains half a molecule arranged around a two-fold rotation axis parallel to the short *b* axis through Mo(1).

Both complexes of **3b** and **3b'** are distorted octahedral dioxomolybdenum(VI) complexes. The most striking structural feature of **3b'** is the very long Mo-N(oxazoline) distance Mo(1)-N(13) of 2.3570(13) Å compared to only 2.144(10) Å in **3b**. This can be explained by the strong *trans*-effect of the terminal oxo ligands (Fig. 3 and Table 3).

Our results should be compared to the previously published dioxomolybdenum(VI) complex equipped with the oxazoline ligand (Fig. 4). Interestingly, the related phenolate-oxazoline complex to **3a**, $[MoO_2(oz)_2]$ (oz = 2-(4,5-dihydrooxazol-2-yl)phenol), had been isolated and characterized by X-ray crystallography in 2008 [25]. In contrast to **3a**, complex $[MoO_2(oz)_2]$ displayed the N,N-isomer in the solid state. Also, the related phenolate complex to **3b** $[MoO_2(oz^{Me2})]$, containing two methyl groups on each oxazoline ligand, was fully structurally characterized [37]. In contrast to **3b** the N,N-isomer was described as the only observed isomer in the solid state. Also a diasteromeric complex $[MoO_2(oz^*)_2]$ containing the chiral ligand (*R*)-2-(4-ethyl-4,5-dihydrooxazol-2-yl)phenol was obtained with a published yield of 80% (Fig. 4) [23]. For the complex $[MoO_2(oz^*)_2]$ single crystals could be grown containing both the N,N- and the O,O-isomer [23]. Thus exact factors leading to one over the other isomer are still not known.



Scheme 3. Catalytic epoxidation of various olefins.

2.1. Epoxidation of olefins

Complexes **3a** and **3b** were tested as catalysts for the epoxidation of various terminal and internal olefins with *tert*-butylhydroperoxide (TBHP) as oxidant (Scheme 3). Initially the optimal conditions regarding solvent, catalyst and oxidant loading were determined using the substrate cyclooctene. At first, the optimal solvent at different temperatures was determined (Table 4). As an example, the results for **3b** are shown, which are also consistent for **3a**.

The best solvent found for epoxidations was 1,2-dichloroethane (DCE) at 80 °C, where cyclooctene was converted to its epoxide in >95% after 30 min. Next, the optimal catalyst and oxidant loading were tested. The results for **3a** are shown in Fig. 5, the same conditions were found to be optimal for **3b**.

The optimal conditions with regards to atom economy and reaction time were found with 0.05 mol% of catalyst and 2 equiv. of TBHP in DCE at 80 °C. Under these conditions a conversion of >95% of cyclooctene was achieved within 90 min. A similar result was obtained for **3b** under the same conditions. With the optimized reaction conditions a set of ten different terminal and internal olefins were tested to further explore the reactivity profile of **3a-b**. Full details for the catalytic experiments are given in the Section 4.

Complexes **3a** and **3b** are catalytically active in the epoxidation of various internal as well as terminal olefins. Internal olefins (Table 1, Table 3, Table 5 entries 1, 3 and 5) are converted with high yields and selectivities to their respective epoxides. For the standard substrate cyclooctene, TOF of 9500 h^{-1} can be achieved. Even with an electron poor terminal olefin like allylphenylether (entry 6) complexes **3a-b** show activity. Styrene (entry 4), which is prone to further unwanted ring-opening reactions after epoxidation, is converted with high selectivities of >90%. The sterically demanding substrates *cis*- and *trans*-stilbene (entries 7 and 8) are also epoxidized in good yields and high selectivities. α-Terpineol and *R*-(+)-limonene are epoxidized unselectively at 80 °C in DCE (entries 9 and 11). However, if the reaction temperature is lowered to 55 °C, both substrates are converted with high selectivities (entries 10 and 12).

Finally we investigated the stability of the catalysts **3a-b** by performing a repeated addition experiment. Under the optimized conditions for epoxidation of cyclooctene (0.05 mol% **3a** or **3b**/2 equiv. TBHP in DCE at 80 °C) aliquots for GC–MS were withdrawn after 60 min and new substrate and TBHP were added. This was repeated three times.

As shown in Fig. 6 the catalyst activity decreases after the second addition and drops further after the third addition of cyclooctene. This could possibly be due to thermal instability of complexes

Table 2
Selected bond distances and angles of **3a**.

Bond distances	(Å)	Bond angles	(°)
Mo(1)-O(4)	1.7088(12)	O(4)-Mo(1)-O(2)	101.51(6)
Mo(1)-O(2)	1.7140(11)	O(2)-Mo(1)-O(21)	162.87(5)
Mo(1)-O(21)	2.0630(11)	O(4)-Mo(1)-O(41)	161.35(5)
Mo(1)-O(41)	2.0651(12)	N(33)-Mo(1)-N(13)	165.93(5)
Mo(1)-N(33)	2.1408(14)	O(41)-Mo(1)-N(33)	78.96(5)
Mo(1)-N(13)	2.1478(13)	O(21)-Mo(1)-N(13)	79.34(5)

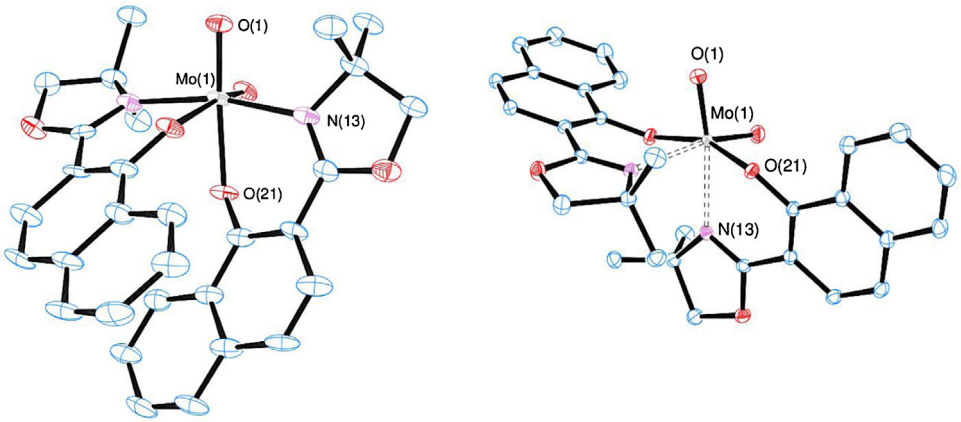


Fig. 3. Molecular structures of **3b** (left) and **3b'** (right) showing the atomic numbering scheme. Probability ellipsoids are drawn at the 50% level; H atoms are omitted for clarity.

Table 3
Selected bond distances and angles of **3b** and **3b'**.

Bond distances (Å)	**3b**	**3b'**	Bond angles (°)	**3b**	**3b'**
Mo(1)-O(1)	1.695(8)	1.7061(11)	O(1)-Mo(1)-O(1)[a]	103.3(5)	106.16(8)
Mo(1)-O(21)	2.078(8)	1.9519(11)	O(1)-Mo(1)-O(21)	164.5(3)	95.80(5)
Mo(1)-N(13)	2.144(10)	2.3570(13)	N(13)-Mo(1)-N(13)[a]	165.0(5)	79.67(6)
			O(21)-Mo(1)-O(21)[a]	78.5(4)	157.90(7)

[a] Symmetry transformations used to generate equivalent atoms: 3/2-*x*, y, 3/2-*z*

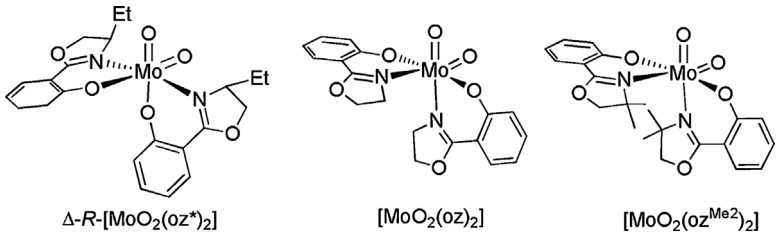


Fig. 4. Previously published and structurally characterized dioxomolybdenum(VI) complexes [23,25,37].

3a-b at 80 °C or as the increasing concentration of *tert*-butanol in the reaction mixture inhibits catalysis.

Overall both complexes **3a-b** show a very similar catalytic activity in the epoxidation of various olefins. Apparently the four methyl groups on the oxazoline moieties in **3b** compared to **3a** have negligible influence on the catalysis. Also with regard to previously published aryloxide–oxazoline complexes the results obtained in our study are comparable. For example, very similar activities for the same substrates were obtained for the phenolate–oxazoline complex $[MoO_2(oz)_2]$. It is feasible that the steric influence of

Table 4
Conversion of cyclooctene to cyclooctane oxide in different solvents.

(min)	Benzene, 55 °C (%)[b]	Toluene, 55 °C (%)[b]	$CHCl_3$, 55 °C (%)[b]	DCE[a], 55 °C (%)[b]	DCE[a]·80 °C (%)[b]
30	80	77	88	84	>95
60	94	87	96	94	
90	>99	89	>99	97	

Conditions: 0.5 mol% **3b**, 2 equiv. TBHP; conversions were determined via GC–MS using mesitylene as internal standard.
[a] 1,2-Dichloroethane.
[b] Conversion of cyclooctene to cyclooctane oxide.

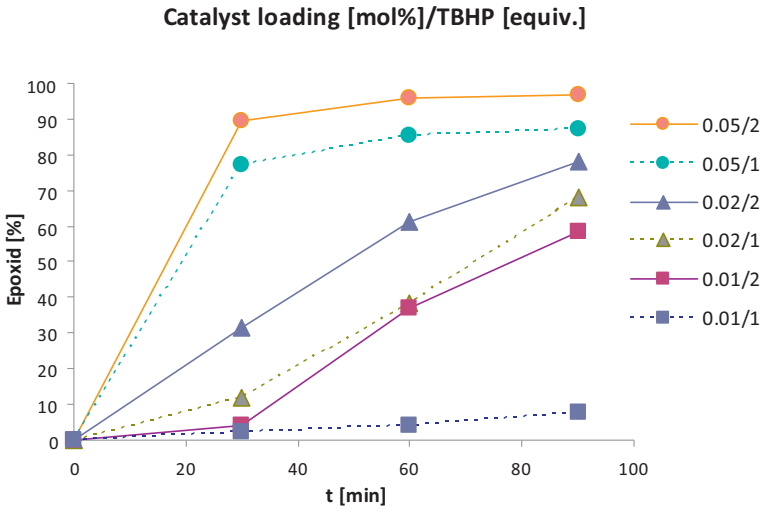
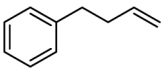
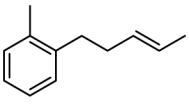
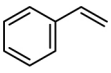
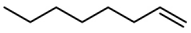
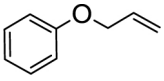
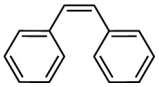
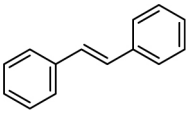
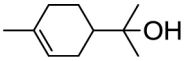
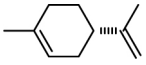


Fig. 5. Testing of different catalyst (**3a**) and oxidant (TBHP) loading in the conversion of cyclooctene in 1,2-dichloroethane at 80 °C.

the ligand coordinated to Mo (naphtholate vs. phenolate) is small. According to the generally accepted mechanism the peroxide coordinates under proton transfer to a terminal oxo ligand to the dioxo-Mo core from the sterically less hindered side [40]. The bulky naphthyl backbone however is located on the opposite side of the Mo atom. Therefore the steric influence of the ligand should be negligible. From an electronic point of view, naphtholate and phenolate substituents are very similar, explaining the overall very

Table 5
Results of epoxidation of various olefins catalyzed by **3a** and **3b**.

		3a				**3b**		
		t (h)	(%)[a]	Sel.[b]	TON	(%)[a]	Sel.[b]	TON
1		1.5	>95	>99	5000	>95	>99	5000
2		21	74	>99	3700	78	>99	3900
3		5	88	>99	4400	88	>99	4400
4		6	76	92	3500	83	90	3730
5		18	76	95	3600	64	89	2840
6		18	19	>99	950	20	>99	1000
7		5	37	>99	1850	44	>99	2200
8		5	42	>99	2100	38	>99	1900
9		5	74	76	2800	71	71	2520
10[c]		5	66	>99	3300	68	>99	3400
11		1	60	64	1920	58	60	1740
12[c]		5	78	>99	3900	87	>99	4350

Conditions: 0.05 mol% catalyst, 2 equiv. TBHP, 1,2-dichloroethane at 80 °C (except entry 10 and 12 at 55 °C).
[a] Conversions determined by GC–MS via peak integration referenced to internal standard mesitylene.
[b] Selectivity towards epoxide product, determined by GC–MS.
[c] Reaction temperature was 55 °C.

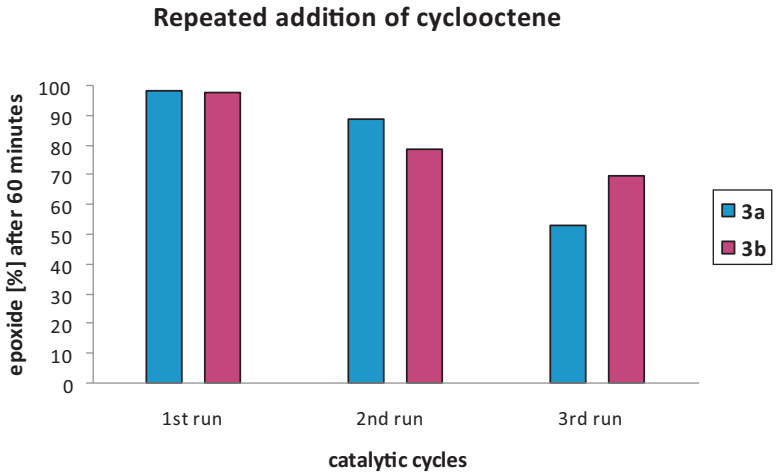


Fig. 6. Repeated addition of cyclooctene and TBHP to catalysts **3a** and **3b**. Conditions used were 0.05 mol% catalyst, 2 equiv. TBHP in DCE at 80 °C.

similar catalytic activities. In contrast, the related chiral complex $[MoO_2(oz^*)_2]$ displayed a rather sluggish behavior as epoxidation catalyst, albeit under different conditions than reported here [24]. Complex $[MoO_2(oz^{Me2})_2]$ was tested in the epoxidation of styrene at room temperature, but showed no activity at all [37].

3. Conclusions

Within this paper we present the synthesis and characterization of two new dioxomolybdenum(VI) complexes **3a-b** equipped with the bidentate monoanionic naphtholate-oxazoline ligands **2a-b**. All analytical data is consistent with the formation of asymmetrically disubstituted complexes. Complexes **3a-b** were also characterized by single crystal X-ray diffraction analysis. In the case of **3b**, both the O,O-isomer (**3b**) as well as the N,N-isomer (**3b'**) could be characterized, although **3b'** was only formed in traces. Furthermore complexes **3a-b** were tested in the catalytic epoxidation of various olefinic substrates. In all cases they showed good to high activity with acceptable selectivities comparable or higher to other published dioxomolybdenum(VI) complexes.

4. Experimental

4.1. General remarks

Unless otherwise specified, all experiments were performed under atmospheric conditions with standard laboratory equipment at the Institute of Chemistry, University of Graz. For the synthesis of **1a-b** please refer to the Supporting Information. All other chemicals and solvents were purchased from commercial sources and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Optics Instrument. Chemical shifts are reported in parts per million (ppm) and referenced to residual protons or carbons in the deuterated solvent. Electron impact mass spectroscopy measurements (EI-MS) were recorded with an Agilent 5973 MSD mass spectrometer with Direct Probe. Gas chromatography mass spectroscopy measurements (GC–MS) have been performed with an Agilent 7890 A (column type Agilent 19091J-433), coupled to a mass spectrometer type Agilent 5975 C. Samples for infrared spectroscopy were measured on a Bruker Optics ALPHA ATR FT-IR Spectrometer. IR bands are reported with wave number (cm^{-1}). Elemental analyses were measured on a Heraeus Vario Elementar automatic analyzer at the Graz University of Technology, Institute of Inorganic Chemistry. Deviations from calculated elemental compositions are due to residual solvent in the sample.

4.2. Single crystal X-ray diffraction analyses

All the measurements were performed using graphite-monochromatized Mo K_α radiation at 100 K. **3a**: $C_{26}H_{20}MoN_2O_6$, M_r 552.38, triclinic, space group P-1, a = 7.2205(3) Å, b = 11.0269(4) Å, c = 13.9798(5) Å, α = 86.8539(14)°, β = 80.1179(13)°, γ = 76.5620(12)°, V = 1066.40(7) Å^3, Z = 2, d_{calc} = 1.720 g cm^{-3}, μ = 0.665 mm^{-1}. A total of 14358 reflections were collected (Θ_{max} = 30.0°), from which 6212 were unique (R_{int} = 0.0253), with 5671 having $I > 2\sigma(I)$. For 322 parameters final R indices of R1 = 0.0263 and wR2 = 0.0669 (GOF = 1.041) were obtained. **3b**: $C_{30}H_{28}MoN_2O_6$, M_r 608.48, monoclinic, space group P 2/n, a = 15.890(3) Å, b = 10.632(2) Å, c = 16.039(3) Å, β = 96.191(8)(, V = 2693.9(9) Å3, Z = 4, d_{calc} = 1.500 g cm^{-3}, μ = 0.534 mm^{-1}. A total of 10725 reflections were collected (Θ_{max} = 26.0°), from which 5256 were unique (R_{int} = 0.0717), with 3092 having $I > 2\sigma(I)$. For 363 parameters final R indices of R1 = 0.0855 and wR2 = 0.2388 (GOF = 1.081) were obtained. **3b'**: $C_{30}H_{28}MoN_2O_6$, Mr 608.48, orthorhombic, space group P b c n, a = 17.4070(6) Å, b = 7.6439(3) Å, c = 19.8304(7) Å, V = 2638.58(17) Å^3, Z = 4, dcalc = 1.532 g cm^{-3}, μ = 0.545 mm^{-1}. A total of 27367 reflections were collected (Θ_{max} = 30.0°), from which 3851 were unique (R_{int} = 0.0353), with 2990 having $I > 2\sigma(I)$. For 183 parameters final R indices of R1 = 0.0244 and wR2 = 0.0659 (GOF = 1.060) were obtained. For full details on data collection and refinement please refer to the Supporting Information. Crystallographic data (excluding structure factors) for the structure of **3a**, **3b** and **3b'** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-940630 (**3a**), CCDC-945467 (**3b**) and CCDC-945466 (**3b'**). Copies of the data can be obtained free of charge on application to: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk]. A summary of the crystallographic data can be found in the Supporting Information which is available online free of charge.

Synthesis of **2a**: a suspension of **1a** (2.31 g, 10 mmol, 1 equiv.) in dichloromethane (50 mL) was cooled to 0 °C. Thionyl chloride (1.79 g, 15 mmol, 1.5 equiv.) was added under Ar slowly over a period of 15 min resulting in a brown solution. The solution was allowed to slowly warm up to room temperature over night. After 12 h stirring at room temperature a suspension was obtained containing crude **2a**·HCl as an off-white solid. The off-white solid was

filtered off, subjected to aqueous work-up with saturated $NaHCO_3$ and dried in vacuo to yield 1.4 g (6.5 mmol, 65%) of **2a** as a pale white solid. ^{1}H NMR (DMSO-d_6, ppm): δ 13.51(s, 1H), 8.29–7.34 (m, 6H), 4.52 (t, J = 9.4 Hz, 2H), 4.09 (t, J = 9.4 Hz, 2H). ^{13}C NMR (DMSO-d_6, ppm): δ 166.40, 158.76, 135.70, 128.60, 127.55, 125.61, 124.30, 123.06, 117.49, 102.68, 67.25, 51.94, 1 C obscured. Selected IR frequencies (cm^{-1}): ~3100 (C—H, aromatic), 1628 ($\nu_{C=N}$). EI-MS: m/z = 213.1 [M^+]. Anal. calcd. for $C_{13}H_{11}NO_2$ (213.23): C 73.23, H 5.20, N 6.57; found: C 72.46, H 5.12, N 6.70

Synthesis of **2b**: a suspension of **1b** (4.86 g, 18.7 mmol, 1.5 equiv) in dichloromethane (100 mL) was cooled to 0 °C. Thionyl chloride (3.35 g, 28.14 mmol, 1 equiv.) was added slowly under Ar over a period of 15 min. The solution was allowed to slowly warm up to room temperature and stirred over night after which the solution was concentrated to a small volume. The crude product of **2b**·HCl was precipitated with ether, subjected to aqueous work-up with saturated $NaHCO_3$ and dried in vacuo to yield 2.34 g (9.72 mmol, 52%) of **2b** as light-brown flakes. ^{1}H NMR ($CDCl_3$, ppm): δ 8.44 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.54 (m, 2H), 7.30 (d, J = 8.7 Hz, 1H), 4.16 (s, 2H, CH_2), 1.45 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 164.53, 158.77, 136.06, 128.23, 127.44, 125.34, 124.79, 123.57, 123.22, 117.85, 103.63, 78.52, 66.66, 28.54, 1 C obscured. Selected IR frequencies (cm^{-1}): 1620 ($\nu_{C=N}$). EI-MS: m/z = 241.1 [M^+]. Anal. calcd. for $C_{15}H_{15}NO_2$ (241.29): C 74.76, H 6.27, N 5.81; found: C 74.01, H 6.22, N 5.99.

Synthesis of [MoO_2(**2a**)$_2$] >(**3a**): to a solution of [MoO_2(acac)$_2$] (0.074 g, 0.23 mmol) in methanol (2 mL) was added a solution **2a** (0.094 g, 0.44 mmol) in methanol (1 mL) and stirred for 1 h. The product precipitated, was filtered, washed with small amounts of methanol and dried in vacuo to yield 0.079 g of **3b** (0.14 mmol, 63%) as an orange–yellowish powder. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **3a** in methanol. ^{1}H NMR (300 MHz, Methanol-d4) δ 8.59 (d, J = 8.1 Hz, 1H), 8.34 (d, J = 7.9 Hz, 1H), 7.76 (m, 2H), 7.56 (m, 6H), 7.25 (d, J = 8.7 Hz, 1H), 7.17 (d, J = 8.9 Hz, 1H), 4.67 (m, 2H), 4.54 (m, 2H), 4.35 (t, J = 9.5 Hz, 3H), 4.14 (t, J = 9.5 Hz, 2H). Due to the low solubility of **3a** no ^{13}C NMR spectrum could be obtained. Selected IR frequencies (cm^{-1}): 1573 ($\nu_{C=N}$), 885, 867 ($\nu_{Mo=O}$). EI-MS: m/z = 554.1 [M^+]; Anal. calcd. for $C_{26}H_{20}MoN_2O_6$ (552.4): C 56.53, H 3.65, N 5.07; found: C 57.87, H 4.65, N 4.53.

Synthesis of [MoO_2(**2b**)$_2$] (**3b**): to a solution of [MoO_2(acac)$_2$] (0.16 g, 0.49 mmol) in methanol (2 mL) was added a solution **2b** (0.21 g, 0.85 mmol) in methanol (2 mL) and stirred for 1 h. The product precipitated, was filtered, washed with small amounts of methanol and dried in vacuo to yield 0.20 g of **3b** (0.33 mmol, 78%) as an orange–yellowish powder. ^{1}H NMR (300 MHz, Methanol-d4) δ 8.57 (d, J = 8.3 Hz, 1H), 8.34 (d, J = 8.3 Hz, 1H), 7.77 (t, J = 7.7 Hz, 2H), 7.57 (m, 6H), 7.29 (d, J = 8.8 Hz, 1H), 7.18 (d, J = 8.8 Hz, 1H), 4.32 (s, 2H), 4.27 (s, 2H) 1.65 (s, 6H), 1.46 (s, 6H). Due to the low solubility of **3b** no ^{13}C NMR spectrum could be obtained. Selected IR frequencies (cm^{-1}): 1573 $\nu_{(C=N)}$, 878, 868 $\nu_{(Mo=O)}$. EI-MS: m/z = 610.1 [M^+]; Anal. calcd. for $C_{30}H_{28}MoN_2O_6$ (608.5): C, 59.21, H 4.64, N 4.60; found: C 59.08, 4.63, 4.53.

4.3. Epoxidation of olefins

In a typical experiment, the respective dioxomolybdenum(VI) complex (0.05 mol%) and olefin (1 mmol, 1 equiv.) were mixed and heated in a Mininert® vial to 55 or 80 °C in 1,2-dichloroethane (1.5 mL), at which time TBHP (363 μl, 2.0 mmol, 2 equiv.) was added. Aliquots for GC–MS (10 μL) were withdrawn, quenched with MnO_2 and diluted with HPLC grade ethyl acetate. The reaction products were analyzed by GC–MS, and quantified via peak integration vs. mesitylene (internal standard).

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