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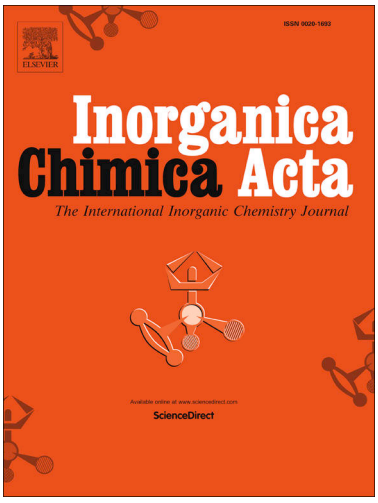

Research paper

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Cis-dioxidomolybdenum(VI) complexes with chiral tetradentate Schiff bases: Synthesis, spectroscopic characterization and catalytic activity in sulfoxidation and epoxidation

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Abstract

New chiral mononuclear *cis*-dioxidomolybdenum(VI) complexes, **MoO_2L^1-MoO_2L^7**, have been synthesized by the reaction of $MoO_2(acac)_2$ with tetradentate Schiff bases derived from various substituted salicylaldehydes and *1S,2S*-(+)-2-amino-1-phenyl-1,3-propanediol. All complexes have been characterized by elemental analysis, circular dichroism, electronic and IR spectral studies. ^{1}H NMR and also two-dimensional (COSY, NOESY and gHSQC) NMR measurements made for **MoO_2L^1-MoO_2L^7** complexes show that Schiff bases are coordinated to MoO_2^{2+} cation creating facial (*fac*) and meridional (*mer*) types of geometrical isomers. Moreover, the catalytic activity studies have been also performed for all complexes in asymmetric sulfoxidation of thioanisole and epoxidation of styrene, cyclohexene and two monoterpenes, i.e. *S*(–)-limonene and (–)-α-pinene, using aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as the oxygen source.

1. Introduction

Chiral Schiff base ligands are considered "privileged ligands" [1] in modern asymmetric catalysis and forming complexes with transition metals as synthetic catalysts are active and moreover enantioselective in many various chemical reactions. Schiff base ligands are able to stabilize many different metals in various oxidation states, controlling their performance in a large variety of useful catalytic transformations. Lately, especially useful are chiral *N*-salicyl-β-amino alcohol Schiff base ligands [2] which are very attractive due to their simple synthesis from naturally available chiral amino acids [3] and which structural and electronic properties can be fine-tuned. They are also a group of ligands which form stable complexes with transition metals with proved catalytic activity, i.e. titanium, vanadium and molybdenum, and therefore widely employed in asymmetric transformations such as oxygen atom transfer (OAT) reactions (epoxidation and sulfoxidation) [4], alkynylation of aldehydes [4a], enantioselective trimethylsilylcyanations [5], oxidation of bromide [6], stereoselective synthesis of cyclic ethers [6,7] oxidative kinetic resolution of α-hydroxy esters [8] or found applications in synthesis of biologically active compounds by multicomponent reactions (MCRs) [9]. Recently, much better yields and selectivities have been achieved towards cyclohexane oxidation using ionic liquid or supercritical carbon dioxide medium in contrast to common solvent [10].

Although different molybdenum complexes have widely studied as catalysts, the chiral ones especially useful in catalytic enantioselective oxidation reactions still remains very limited [11]. Nevertheless, *cis*-dioxidomolybdenum(VI) complexes with tridentate and tetradentate Schiff bases have been successfully employed as catalysts in very efficient epoxidation of olefins (including styrene and cyclohexene) [12-15], oxidation of sulfides to sulfoxides [16-18]. Lately, particular attention has been drawn on monocyclic and bicyclic

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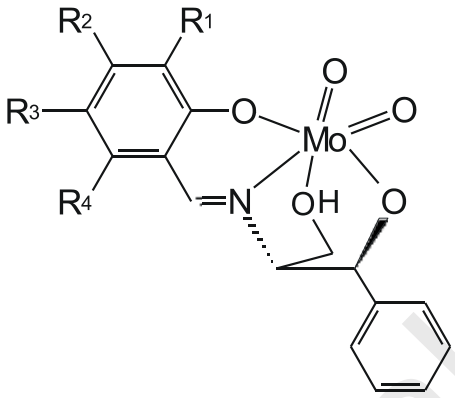
monoterpenes, such as limonene and pinene, which are abundant natural products, but also inexpensive by-product from the citrus fruit juice industry [19] and technical forestry resin or wood pulp by-produced in the manufacture of cellulose [20], respectively.

We have an ongoing interest in the chemistry of dioxidomolybdenum(VI) complexes using different ONO tridentate donor ligands [21, 22]. In this paper we describe new ten *cis*-dioxidomolybdenum(VI) complexes with tetradentate ONOO Schiff base ligands, products of a single condensation of *1S*,*2S*-(+)-2-amino-1-phenyl-1,3-propanediol with salicylaldehyde and its derivatives, presented in Fig. 1. Very detailed investigation of their spectroscopic properties using IR, UV-Vis, circular dichroism, one- and two-dimensional NMR techniques has been also performed. Moreover, their catalytic abilities in enantioselective sulfoxidation of thioanisole and epoxidation of alkenes, i.e. styrene and cyclohexene, and monoterpenes, i.e. *S*(−)-limonene and (−)-α-pinene, in the presence of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide as the terminal oxidant, have been studied.

Figure 1. Structural formulae of dioxidomolybdenum(VI) complexes.



	R1	R2	R3	R4
MoO_2L^1	H	H	H	H
MoO_2L^2	H	H	OCH_3	H
MoO_2L^3	H	H	Br	H
MoO_2L^4	H	H	NO_2	H
MoO_2L^5	H	OH	H	H
MoO_2L^6	$(CH_3)_3C$	H	H	H
MoO_2L^7	H	H	$-(CH)_4-$	

2. Experimental

2.1. Measurements

All chemicals and reagents were obtained from commercial sources and used without further purification. Elemental analyses were performed with a Carlo Erba MOD 1106 instrument. Electronic spectra were measured on a Perkin-Elmer LAMBDA 18 spectrophotometer. CD spectra were recorded on a Jasco J-815 spectropolarimeter. IR spectra of solid samples (KBr pellets) were run on a Bruker IFS 66. NMR spectra were obtained in DMSO-d_6 solutions with a Bruker AVANCE III 700 MHz spectrometer using TMS as a reference. A Shimadzu GC-2025 gas chromatograph with a Zebron ZB-5 capillary column (30 m × 0.25 mm × 0.25 mm) and FID detector were used to during catalytic studies. The identities of the oxidation products have been confirmed by GC-MS model Shimadzu GCMS-QP2010 SE.

2.2. Synthesis of dioxidomolybdenum(VI) complexes

A similar procedure was employed for synthesis of all complexes. To a solution of 1 mmol of *1S,2S*-(+)-2-amino-1-phenyl-1,3-propanediol in MeOH (10 ml) 1 mmol of one of following aromatic *o*-hydroxyaldehyde was added, i.e. salicylaldehyde, 5-methoxysalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, 4-hydroxysalicylaldehyde, 3-*tert*-butylsalicylaldehyde or 2-hydroxy-1-naphthaldehyde in 10 ml of MeOH and reaction mixture was heated with stirring under reflux for 1 h. Then, bis(acetylacetonato)dioxidomolybdenum(VI) (1 mmol) in MeOH (10 ml) was added and stirred at under reflux for next 2 h. After cooling precipitates were separated as yellow solids, filtered off and washed with MeOH.

MoO₂L¹: Yield 82%. *Anal.* Calc. for $C_{16}H_{15}NO_5Mo$: C, 48.4; H, 3.8; N, 3.5. Found: C, 48.3; H, 3.7; N, 3.5%. IR (KBr, cm^{-1}): 3355 (ν_{O-H}); 1633 ($\nu_{C=N}$); 1589, 1480 ($\nu_{C=C}$); 1265 (ν_{C-O}); 926, 883 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 267 (7930), 346 (1630). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 279 (9.13), 349 (5.65). ^{1}H NMR (DMSO-*d*$_6$, ppm) *mer*-isomer (65%): 8.75 (1H, s) (azomethine); 7.61 (1H, dd, ^3J=7.8 Hz, ^4J=1.6 Hz), 7.51 (1H, t, ^3J=7.8 Hz), 7.45 (2H, d, ^3J=7.3 Hz), 7.39 (2H, t, ^3J=7.3 Hz), 7.33 (1H, t, ^3J=7.3 Hz), 6.98 (1H, ov), 6.92 (1H, d, ^3J=9.0 Hz) (aromatic); 5.22 (1H, ov) (hydroxyl); 5.24 (1H, d, ^3J=8.0 Hz), 3.85 (1H, m) (methine); 4.10 (1H, dt, ^3J=12.3 Hz, ^4J=4.0 Hz), 3.60 (1H, dt, ^3J=12.3 Hz, ^4J=5.6 Hz) (methylene); *fac*-isomer (35%): 8.77 (1H, s) (azomethine); 7.65 (1H, dd, ^3J=7.8 Hz, ^4J=1.6 Hz), 7.51 (1H, t, ^3J=7.8 Hz), 7.45 (2H, ov), 7.39 (2H, ov), 7.33 (1H, ov), 7.00 (1H, ov), 6.94 (1H, d, ^3J=9.0 Hz) (aromatic); 5.65 (1H, d, ^3J=4.3 Hz) (hydroxyl); 4.07 (1H, ov), 4.05 (1H, ov) (methine); 4.73 (1H, dd, ^3J=9.0 Hz, ^4J=4.3 Hz), 4.07 (1H, ov) (methylene).

MoO₂L²: Yield 86%. *Anal.* Calc. for $C_{17}H_{17}NO_6Mo$: C, 47.8; H, 4.0; N, 3.3. Found: C, 47.7; H, 3.9; N, 3.3%. IR (KBr, cm^{-1}): 3416 (ν_{O-H}); 1638 ($\nu_{C=N}$); 1612, 1483 ($\nu_{C=C}$); 1279 (ν_{C-O}); 925, 898 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 274 (6650), 375 (1750). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 279 (10.46), 383 (4.84). ^{1}H NMR (DMSO-*d*$_6$, ppm) *mer*-isomer (65%): 8.75 (1H, s) (azomethine); 7.45 (2H, d, ^3J=7.3 Hz), 7.40 (2H, t, ^3J=7.3 Hz), 7.33 (1H, t, ^3J=7.3 Hz), 7.20 (1H, d, ^3J=3.2 Hz), 7.13 (1H, t, ^3J=3.2 Hz), 6.87 (1H, d, ^3J=9.0 Hz) (aromatic); 5.14 (1H, t, ^3J=5.1 Hz) (hydroxyl); 5.21 (1H, d, ^3J=8.0 Hz), 3.81 (1H, m) (methine); 3.96 (1H, dt, ^3J=12.2 Hz, ^4J=3.8 Hz), 3.61 (1H, dt, ^3J=12.2 Hz, ^4J=5.5 Hz) (methylene); 3.77 (3H, s) (methoxy); *fac*-isomer (35%): 8.77 (1H, s) (azomethine); 7.43 (2H, ov), 7.39 (2H, ov), 7.34 (1H, ov), 7.25 (1H, d, ^3J=3.2 Hz), 7.15 (1H, t, ^3J=3.2 Hz), 6.89 (1H, d, ^3J=9.0 Hz) (aromatic); 5.63 (1H, d, ^3J=4.4 Hz) (hydroxyl); 4.07 (1H, ov), 4.05 (1H, ov) (methine); 4.73 (1H, dd, ^3J=9.1 Hz, ^4J=4.4 Hz), 4.02 (1H, dd, ^3J=10.2 Hz, ^4J=4.9 Hz) (methylene); 3.78 (3H, s) (methoxy).

MoO₂L³: Yield 77%. *Anal.* Calc. for $BrC_{16}H_{14}NO_5Mo$: C, 40.4; H, 3.0; N, 2.9. Found: C, 40.2; H, 3.1; N, 3.0%. IR (KBr, cm^{-1}): 3405 (ν_{O-H}); 1634 ($\nu_{C=N}$); 1613, 1494 ($\nu_{C=C}$); 1235 (ν_{C-O}); 931, 906 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 268 (8310), 355 (1640). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 278 (9.54), 359 (5.26). ^{1}H NMR (DMSO-*d*$_6$, ppm) *mer*-isomer (65%): 8.74 (1H, s) (azomethine); 7.85 (1H, d, ^3J=2.6 Hz), 7.62 (1H, t, ^3J=2.6 Hz), 7.45 (2H, d, ^3J=7.3 Hz), 7.40 (2H, t, ^3J=7.3 Hz), 7.34 (1H, t, ^3J=7.3 Hz), 6.90 (1H, d, ^3J=8.8 Hz) (aromatic); 5.14 (1H, t, ^3J=5.3 Hz) (hydroxyl); 5.28 (1H, d, ^3J=8.0 Hz), 3.84 (1H, m) (methine); 3.98 (1H, dt, ^3J=12.3 Hz, ^4J=4.0 Hz), 3.59 (1H, dt, ^3J=12.3 Hz, ^4J=5.6 Hz) (methylene); *fac*-isomer (35%): 8.77 (1H, s) (azomethine); 7.90 (1H, d, ^3J=2.6 Hz), 7.64 (1H, t, ^3J=2.6 Hz), 7.46 (2H, ov), 7.38 (2H, ov), 7.34 (1H, ov), 6.92 (1H,

d, ^3J=8.8 Hz) (aromatic); 5.68 (1H, d, ^3J=4.4 Hz) (hydroxyl); 4.09 (1H, ov), 4.08 (1H, ov) (methine); 4.73 (1H, dd, ^3J=9.0 Hz, ^4J=4.4 Hz), 4.07 (1H, ov) (methylene).

MoO_2L^4: Yield 83%. *Anal.* Calc. for $C_{16}H_{14}N_2O_7Mo$: C, 43.5; H, 3.2; N, 6.3. Found: C, 43.6; H, 3.3; N, 6.3%. IR (KBr, cm^{-1}): 3424 (ν_{O-H}); 1623 ($\nu_{C=N}$); 1606, 1509 ($\nu_{C=C}$); 1551, 1336 (ν_{NO2}); 1509 ($\nu_{C=C}$); 1249 (ν_{C-O}); 915, 897 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 330 (14440). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 277 (8.75), 328 (7.64). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 9.05 (1H, s) (azomethine); 8.72 (1H, d, ^3J=2.6 Hz), 7.64 (1H, t, ^3J=2.6 Hz), 7.47 (2H, d, ^3J=7.3 Hz), 7.43 (2H, t, ^3J=7.3 Hz), 7.36 (1H, t, ^3J=7.2 Hz), 7.17 (1H, d, ^3J=8.7 Hz) (aromatic); 5.17 (1H, t, ^3J=5.2 Hz) (hydroxyl); 5.30 (1H, d, ^3J=8.2 Hz), 3.86 (1H, m) (methine); 3.99 (1H, dt, ^3J=12.2 Hz, ^4J=4.0 Hz), 3.61 (1H, dt, ^3J=12.3 Hz, ^4J=5.6 Hz) (methylene); *fac*-isomer (35%): 9.08 (1H, s) (azomethine); 8.76 (1H, d, ^3J=2.6 Hz), 7.67 (1H, t, ^3J=2.6 Hz), 7.48 (2H, ov), 7.37 (2H, ov), 7.33 (1H, ov), 7.19 (1H, d, ^3J=8.7 Hz) (aromatic); 5.71 (1H, d, ^3J=4.3 Hz) (hydroxyl); 4.10 (1H, ov), 4.09 (1H, ov) (methine); 4.76 (1H, dd, ^3J=9.0 Hz, ^4J=4.3 Hz), 4.10 (1H, ov) (methylene).

MoO_2L^5: Yield 77%. *Anal.* Calc. for $C_{16}H_{15}NO_6Mo$: C, 46.5; H, 3.7; N, 3.4. Found: C, 46.5; H, 3.8; N, 3.5%. IR (KBr, cm^{-1}): 3308 (ν_{O-H}); 1638 ($\nu_{C=N}$); 1604, 1477 ($\nu_{C=C}$); 1219 (ν_{C-O}); 932, 902 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 287 (8280), 338 (2970). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 294 (8.35), 344 (7.76). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 10.28 (1H, s) (hydroxyl); 8.61 (1H, s) (azomethine); 7.43 (2H, d, ^3J=7.3 Hz), 7.38 (2H, t, ^3J=7.3 Hz), 7.31 (1H, t, ^3J=7.3 Hz), 7.25 (1H, t, ^3J=7.5 Hz), 6.41 (1H, d, ^3J=8.3 Hz), 6.24 (1H, s) (aromatic); 5.15 (1H, t, ^3J=5.2 Hz) (hydroxyl); 5.28 (1H, d, ^3J=8.2 Hz), 3.86 (1H, m) (methine); 3.97 (1H, dt, ^3J=12.1 Hz, ^4J=4.1 Hz), 3.59 (1H, dt, ^3J=12.3 Hz, ^4J=5.6 Hz) (methylene); *fac*-isomer (35%): 10.31 (1H, s) (hydroxyl); 8.63 (1H, s) (azomethine); 7.42 (2H, ov), 7.37 (2H, ov), 7.33 (1H, ov), 7.27 (1H, t, ^3J=7.5 Hz), 6.43 (1H, d, ^3J=8.3 Hz), 6.27 (1H, s) (aromatic); 5.70 (1H, d, ^3J=4.3 Hz) (hydroxyl); 4.11 (1H, ov), 4.10 (1H, ov) (methine); 4.74 (1H, dd, ^3J=9.0 Hz, ^4J=4.3 Hz), 4.10 (1H, ov) (methylene).

MoO_2L^6: Yield 81%. *Anal.* Calc. for $C_{20}H_{23}NO_5Mo$: C, 53.0; H, 5.1; N, 3.1. Found: C, 53.2; H, 5.0; N, 3.0%. IR (KBr, cm^{-1}): 3416 (ν_{O-H}); 1630 ($\nu_{C=N}$); 1592, 1494 ($\nu_{C=C}$); 1280 (ν_{C-O}); 914, 878 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 271 (8110), 353 (1670). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 282 (10.60), 358 (5.35). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 8.73 (1H, s) (azomethine); 7.42 (2H, d, ^3J=7.3 Hz), 7.38 (2H, t, ^3J=7.3 Hz), 7.31 (1H, t, ^3J=7.3 Hz), 7.15 (1H, d, ^3J=7.6 Hz), 7.09 (1H, d, ^3J=7.6 Hz), 6.82 (1H, t, ^3J=7.6 Hz) (aromatic); 5.12 (1H, t, ^3J=5.1 Hz) (hydroxyl); 5.20 (1H, d, ^3J=7.9 Hz), 3.79 (1H, m) (methine); 3.94 (1H, dt, ^3J=12.2 Hz, ^4J=3.9 Hz), 3.60 (1H, dt, ^3J=12.2 Hz, ^4J=5.4 Hz) (methylene); 1.41 (9H, s) (*tert*-butyl); *fac*-isomer (35%): 8.75 (1H, s) (azomethine); 7.41 (2H, ov), 7.37 (2H, ov), 7.32 (1H, ov), 7.17 (1H, d, ^3J=7.6 Hz), 7.11 (1H, d, ^3J=7.6 Hz), 6.84 (1H, t, ^3J=7.6 Hz) (aromatic); 5.62 (1H, d, ^3J=4.4 Hz) (hydroxyl); 4.08 (1H, ov), 4.07 (1H, ov) (methine); 4.71 (1H, dd, ^3J=9.0 Hz, ^4J=4.2 Hz), 4.01 (1H, dd, ^3J=10.1 Hz, ^4J=4.9 Hz) (methylene); 1.43 (9H, s) (*tert*-butyl).

MoO_2L^7: Yield 80%. *Anal.* Calc. for $C_{20}H_{17}NO_5Mo$: C, 53.7; H, 3.8; N, 3.1. Found: C, 53.5; H, 3.7; N, 3.2%. IR (KBr, cm^{-1}): 3388 (ν_{O-H}); 1630 ($\nu_{C=N}$); 1609, 1497 ($\nu_{C=C}$); 1250 (ν_{C-O}); 914, 889 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 272 (6820), 308 (6300), 381 (2460). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 279 (3.29), 303 (3.02),

380 (6.21). ^{1}H NMR (DMSO-d_6, ppm) *mer*-isomer (65%): 9.57 (1H, s) (azomethine); 8.48 (1H, d, ^{3}J=8.5 Hz), 8.09 (1H, d, ^{3}J=9.0 Hz), 7.93 (1H, d, ^{3}J=8.1 Hz), 7.65 (1H, t, ^{3}J=7.3 Hz), 7.46 (1H, t, ^{3}J=7.3 Hz), 7.40 (2H, d, ^{3}J=7.3 Hz), 7.36 (2H, t, ^{3}J=7.3 Hz), 7.30 (1H, t, ^{3}J=7.3 Hz), 7.18 (1H, d, ^{3}J=9.0 Hz) (aromatic); 5.15 (1H, t, ^{3}J=5.1 Hz) (hydroxyl); 5.23 (1H, d, ^{3}J=7.9 Hz), 3.81 (1H, m) (methine); 3.97 (1H, dt, ^{3}J=12.1 Hz, ^{4}J=3.9 Hz), 3.63 (1H, dt, ^{3}J=12.1 Hz, ^{4}J=5.3 Hz) (methylene); *fac*-isomer (35%): 9.59 (1H, s) (azomethine); 8.50 (1H, d, ^{3}J=8.5 Hz), 8.11 (1H, d, ^{3}J=9.0 Hz), 7.96 (1H, d, ^{3}J=8.1 Hz), 7.67 (1H, t, ^{3}J=7.3 Hz), 7.48 (1H, t, ^{3}J=7.3 Hz), 7.39 (2H, ov), 7.35 (2H, ov), 7.32 (1H, ov), 7.20 (1H, d, ^{3}J=9.0 Hz) (aromatic); 5.64 (1H, d, ^{3}J=4.3 Hz) (hydroxyl); 4.11 (1H, ov), 4.09 (1H, ov) (methine); 4.74 (1H, dd, ^{3}J=9.0 Hz, ^{4}J=4.2 Hz), 4.04 (1H, dd, ^{3}J=10.2 Hz, ^{4}J=4.9 Hz) (methylene).

2.3. Catalytic activity

2.3.1. Sulfoxidation reactions

All dioxidomolybdenum(VI) complexes have been tested as catalysts for sulfoxidation of thioanisole in the presence of aqueous 30% H_2O_2 or 5.5 M decane solution of *tert*-butyl hydroperoxide (TBHP) as the terminal oxidant. The catalyst, thioanisole and oxidant amounts were in 0.01, 1 and 1.1 mmol, respectively. The reactions were run in CH_2Cl_2 and MeOH (7:3) solution for a better mixing of the aqueous oxidant with the halogenated solvent [23] and enhancing the yield and selectivity of sulfoxide by protic solvent [24]. After the appropriate reaction time, the solution was quenched with 3 ml of sodium sulfite solution (0.1 M), extracted with ethyl acetate and organic layers were evaporated to dryness. The yield and reaction rates were estimated on the basis of the integrated intensities of substrate and product signals in $CDCl_3$ using ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. After addition of chiral shift reagent - Eu(hfc)$_3$ [25] the enantiomeric excesses of methyl phenyl sulfoxide were calculated.

2.3.2. Epoxidation reactions

The catalytic abilities of all complexes were studied for epoxidation of alkenes, i.e. styrene and cyclohexene, and monoterpenes, i.e. *S*(–)-limonene and (–)-α-pinene, using aqueous 30% H_2O_2 or 5.5 M decane solution of *tert*-butyl hydroperoxide. Different amounts of catalysts and oxidants were also tested to optimize reaction conditions. All reactions were run in 1,2-dichloroethane (DCE) at 80 °C and monitored by GC using 1:100:200 molar ratio of catalyst, substrate and oxidant, respectively. The yields were recorded as GC yield based on the starting substrate. The identity of oxidation products were confirmed by GC-MS.

3. Results and discussion

3.1. IR spectra

The IR spectra for **MoO_2L^1-MoO_2L^7** complexes exhibit medium bands centered at 3308-3424 cm^{-1} and are assigned to ν(O-H) vibrations of coordinated hydroxyl group. The characteristic imine C=N band, which exist at 1623-1638 cm^{-1} indicating the presence of azomethine nitrogen atom of all Schiff base ligands coordinated to the molybdenum ion [26, 27]. Moreover, the appearance of ν(C-O) bands at 1219-1280 cm^{-1} also suggest the coordination alkoxide ions and OH groups. In case of **MoO_2L^4**, with nitro substituent attached to aromatic ring of salicylaldehyde moiety, asymmetric and symmetric N-O stretches have been found at 1551 and 1336 cm^{-1}, respectively. Finally, a pairs of sharp and strong bands at

914-932 and 878-906 cm^{-1} due to the streching ν_{asym}(O=Mo=O) and ν_{sym}(O=Mo=O) modes, respectively, clearly confirm the presence of a *cis*-[$Mo^{VI}O_2$] structure [28].

3.2. Electronic and circular dichroism spectra

Electronic absorption and circular dichroism spectra of *cis*-dioxidomolybdenum(VI) complexes were recorded in spectroscopic grade DMSO. The UV-Vis spectra display intraligand π-π^* transitions in 267-287 nm region. The low-energy transitions appear between 338-381 nm are assigned to a ligand-to-metal charge transfer (LMCT) transition arising from the phenolate oxygen p_π orbital to an empty d orbital of molybdenum atom [29]. The **MoO_2L^4** compound is exception to this rule and exhibit only one strong broad band at 330 nm (ε_{max} = 14440) and the spectrum of **MoO_2L^7** with naphthyl ring displays additional band at 308 nm (ε_{max} = 6300). The circular dichroism spectra revealed the same bands in 277-294 nm and 328-383 nm region of the same origin as electronic spectra with very strong positive sign of the Cotton effects.

3.3. NMR measurements

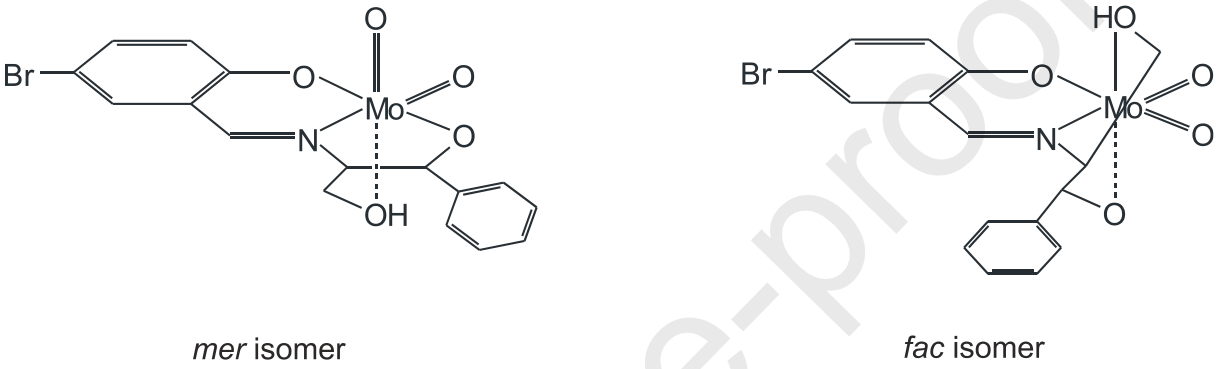
The one- (^{1}H) and two-dimensional (COSY, NOESY, gHSQC) NMR spectra of dioxidomolybdenum(VI) Schiff base complexes were recorded in DMSO-d_6. The ^{1}H spectra of all complexes have shown the presence of azomethine proton signals proving condensation reaction between all salicylaldehyde derivatives with *1S,2S*-(+)-2-amino-1-phenyl-1,3-propanediol. Complete assignments and identification of all proton and carbon signals and establishing a connection and proximity between all protons and their attachment to carbon atoms have been achieved using two-dimensional NMR experiments and are listed in Experimental section.

We reported earlier that *cis*-dioxidomolybdenum(VI), but also oxidovanadium(V) and *cis*-dioxidovanadium(V) complexes with unsymmetrical tridentate Schiff base ligands, products of monocondensation reaction of salicylaldehyde and its derivatives with amino alcohols and diamines, have been proven to possess a rigid and nearly planar backbone composed of three donor centers established by the Schiff base linkage, which prefer only a meridional coordination mode [22, 30]. Moreover, such complexes with similar high-denticity ligands, i.e. pentadentate Schiff bases also revealed only meridional arrangement of coordination sites [31]. It was possible to observe in solution a second isomer in facial coordination arrangement but after reduction of imine functionality obtaining flexible amine ligand system [32]. In case of **MoO_2L^1-MoO_2L^7** complexes their Schiff bases are coordinated to MoO_2^{2+} cation creating meridional (*mer*) and facial (*fac*) types of geometrical isomers, respectively (Fig. 2). Liimatainen *et al.* [33] reported crystallization of racemic **MoO_2L^1** and X-ray analysis revealed its molecular structure, which, in contrast to our chiral **MoO_2L^1** complex, possess one hydroxyl group uncoordinated and a methanol molecule completes coordination sphere. Moreover, as expected only meridional isomer is present and chemical shifts in ^{1}H NMR spectrum are in good agreement with our results.

The ^{1}H NMR spectra of **MoO_2L^1-MoO_2L^7** show that all protons of both isomers are chemically different giving rise to two sets of signals in 65:35 ratio and the resonances of the *mer*-isomers are generally observed at lower frequencies. The chemical shift differences between the two methine protons of the amino alcohol chelate rings of the *fac*-isomers are rather very small. Whereas for the *mer*-isomers a distinct separation between the two resonances is observed (almost 1.5 ppm). On the other hand, the separations between the methylene protons are for the *fac*-isomers *ca.* 0.3 ppm bigger and moreover, signal of the proton of coordinated hydroxyl group is a doublet. Furthermore, taking **MoO_2L^3** as an

example, COSY spectrum show cross-peak between coordinated hydroxyl proton doublet at 5.68 pm only with one of the methylene protons at 4.73 ppm, but the hydroxyl proton triplet of *mer*-isomer (5.14 ppm) reveals cross-peaks with both methylene protons at 3.98 and 3.59 ppm. In case of both isomers the methylene protons show unambiguously connection with methine proton (at 3.84 for *mer*-isomer and 4.09 for *fac*-isomer) neighboring with azomethine nitrogen. Additionally, NOESY spectrum reveals spacial proximity between azomethine proton with signal at 8.74 ppm in case of *mer*-isomer and one of the aromatic proton (doublet signal at 7.85 ppm), the methine proton (at 3.84 ppm) and both methylene protons (at 3.98 and 3.59 ppm), whereas the only one cross-peak with methylene proton (signal at 4.07 ppm) is present for the *fac*-isomer.

Figure 2. Facial (*fac*) and meridional (*mer*) geometrical isomers of **MoO_2L^3** complex.



3.4. Catalytic activity studies

3.4.1. Enantioselective sulfoxidation of thioanisole

Catalytic activities of all *cis*-dioxidomolybdenum(VI) complexes **MoO_2L^1-MoO_2L^7** were tested for sulfoxidation of thioanisole with a slight excess (1.1 equivalents) of *tert*-butyl hydroperoxide (TBHP) or aqueous 30% H_2O_2 as the terminal oxidants (Fig. 3). The reactions were run in $CDCl_3$ at different temperatures (25 and −20 °C) with optimized amounts of the catalysts (1 mol%) and under these conditions no overoxidation to the corresponding sulfone was detected. In control experiments carried out without any molybdenum(VI) Schiff base catalysts present or in the presence of $MoO_2(acac)_2$ no significant amounts of reactions products have been detected. All studied complexes presented practically similar overall catalytic ability, suggesting that they may involve the same catalytic species.

Overall conversion of thioanisole to methyl phenyl sulfoxide in the presence of all molybdenum(VI) catalysts was slightly higher using 30% H_2O_2 as the oxidant, in comparison to TBHP (Table 1). In all cases the *R*-configured sulfoxides were obtained with enantiomeric excesses from 20 to 29% using 30% H_2O_2 (entries 1-10) and 13-26% when TBHP was employed as the terminal oxidant (entries 11-20). These results clearly show that catalytic activities of all complexes in sulfoxidation of thioanisole are lower with TBHP than in the analogous reactions involving aqueous 30% H_2O_2. The reaction temperature seemed to have some effect on the observed enantioselectivity and a slight increase in the enantiomeric excess with lower reaction temperature was noticed. For example in the case of **MoO_2L^2**, **MoO_2L^4** and **MoO_2L^6** the decrease in the reaction temperature was accompanied with longer reaction time but also with a slight increase in enantioselectivity and without additional sulfone production (entries 3, 6, 9, 13, 16 and 19).

It is noteworthy to mention that in case of studied molybdenum(VI) complexes the best enantioselectivities were achieved with catalysts possessing high electron-donating substituents where a higher electron density on the phenolate oxygen in salicylaldimine moiety helps to improve attainment of sufficient nucleophilicity by the metal centre. Mimoun *et al.* reported [34] that sufficient nucleophilic center in d^0 metal catalysts has significant importance for a number of types of organic substrates used in catalytic oxidation processes.

Figure 3. Sulfoxidation of thioanisole catalyzed by *cis*-dioxidomolybdenum(VI) complexes.

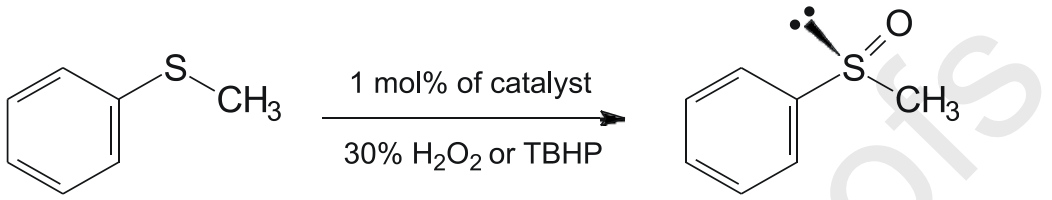


Table 1. Asymmetric sulfoxidation of thioanisole in the presence of molybdenum(VI) Schiff base complexes as catalysts.

entry	catalyst	oxidant	*T* (°C) [a]	yield (%)	*ee* (%) [b]
1	**MoO_2L^1**	H_2O_2	25	78	21
2	**MoO_2L^2**	H_2O_2	25	80	25
3	**MoO_2L^2**	H_2O_2	–20	84	29
4	**MoO_2L^3**	H_2O_2	25	85	23
5	**MoO_2L^4**	H_2O_2	25	81	22
6	**MoO_2L^4**	H_2O_2	–20	87	27
7	**MoO_2L^5**	H_2O_2	25	77	20
8	**MoO_2L^6**	H_2O_2	25	79	21
9	**MoO_2L^6**	H_2O_2	–20	84	25
10	**MoO_2L^7**	H_2O_2	25	80	20
11	**MoO_2L^1**	TBHP	25	77	17
12	**MoO_2L^2**	TBHP	25	82	22
13	**MoO_2L^2**	TBHP	–20	85	26
14	**MoO_2L^3**	TBHP	25	79	13
15	**MoO_2L^4**	TBHP	25	82	14
16	**MoO_2L^4**	TBHP	–20	88	19
17	**MoO_2L^5**	TBHP	25	84	15
18	**MoO_2L^6**	TBHP	25	80	20
19	**MoO_2L^6**	TBHP	–20	86	23
20	**MoO_2L^7**	TBHP	25	79	19

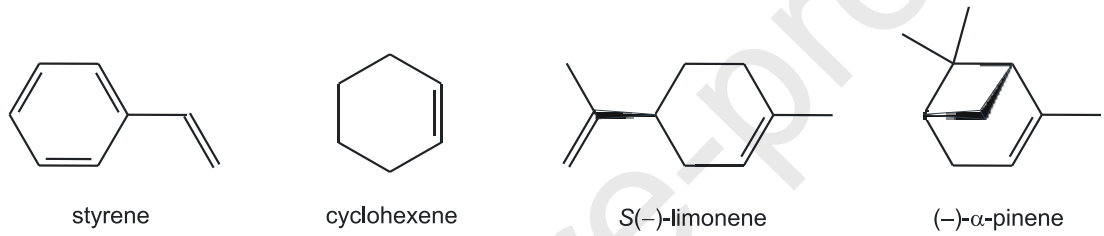
[a] Optimized reaction times were 1.5 h at 25 °C and 5 h at –20 °C. [b] In all cases enantiomeric excess of methyl phenyl sulfoxide was found to be in *R* configuration.

3.5.2. Epoxidation of alkenes and monoterpenes

Catalytic abilities of chiral *cis*-dioxidomolybdenum(VI) complexes with tetradentate Schiff bases, **MoO_2L^1-MoO_2L^7** have been studied in epoxidation of alkenes, such as styrene and cyclohexene, but also monoterpenes, which are cyclohexene naturally occurring derivatives, i.e. *S*(–)-limonene and (–)-α-pinene (Fig. 4). As the terminal oxidants 30%

aqueous H_2O_2 or *tert*-butyl hydroperoxide (TBHP) were used and 1,2-dichloroethane (DCE) was found to be the most efficient solvent with regards to other solvents like toluene, acetonitrile, ethanol, methanol, $CHCl_3$ and CH_2Cl_2. The poorer yields obtained especially with latter ones may be probably caused by the lower reaction temperature for their reflux conditions. Considering our observations in conversion and selectivity, higher reaction temperature, i.e. 80 °C, has an overall benefit to achieve the best yields for all epoxidation reactions which required 1 h to reach completion. Similar conclusions that higher reactions temperature can be responsible for obtaining better yields and reaction rates have been also drawn previously [35]. In order to achieve suitable reaction conditions for a maximum oxidative conversion the influence of different reaction parameters were taken into account, i.e. amount of catalyst (0.5, 1, 2 and 3 mol% loadings) and oxidant molar ratios to substrate (1:1, 2:1, 3:1 and 4:1). It was observed that using 1 mol% of each catalyst with 2:1 molar ratio of both oxidants to all substrates were sufficient to run the epoxidations and an increase in these ratios did not noticeably affect the reaction rates.

Figure 4. Substrates used for catalytic oxidation studies.



As we have previously reported [21, 22], the oxidation of styrene with catalytic amounts of dioxidomolybdenum(VI) Schiff base complexes using aqueous 30% H_2O_2 or TBHP as the terminal oxidants generally can result in five oxidation products, i.e. styrene oxide, benzaldehyde, benzoic acid, phenylacetaldehyde and 1-phenylethane-1,2-diol. Formation of as many as five products with similar molybdenum catalysts has been also observed earlier [36]. Styrene oxide can be formed in the first step, but further reaction, via nucleophilic attack of the oxidant to styrene oxide followed by the cleavage of the intermediate hydroperoxystyrene, is very fast, converting the product into benzaldehyde [37], which can be also further oxidized to benzoic acid. Moreover, the direct formation of benzaldehyde can be also facilitated via a radical mechanism by direct oxidative cleavage of the styrene side-chain double bond. The presence of water, in case of aqueous 30% H_2O_2, can be blamed for the decomposition of the catalyst and thus the very low conversion of styrene. Moreover, it can be also responsible for the formation of 1-phenylethane-1,2-diol by the hydrolysis of styrene oxide and finally, styrene oxide isomerisation can lead to the formation of phenylacetaldehyde.

During our studies it was observed that the epoxidation of styrene by aqueous 30% H_2O_2 give as expected low conversions (16-21%), but when TBHP is added to reaction mixtures in non-aqueous environment, the conversions of styrene increase significantly to 66-82%. These reactions carried out with both oxidants lead to the formation of styrene oxide as a major product along with only small amounts of benzaldehyde and without any additional by-products (Table 2, entries 1-10). Similar conversion (71-75%) and excellent epoxide selectivity were obtained by Judmaier *et al.* [38] with 0.5 mol% of molybdenum(VI) Schiff base catalysts loading in 5 h of reaction time, but in chloroform at 50 °C.

The epoxidation of cyclohexene with catalytic amounts of *cis*-dioxidomolybdenum(VI) Schiff base complexes generally results in epoxidation products, i.e.

cyclohexene oxide and, after its eventual hydrolysis, cyclohexene-1,2-diol, but also the formation of allylic oxidation products is possible, i.e. 2-cyclohexen-1-ol and 2-cyclohexen-1-one (Fig. 5). Mono- and bicyclic monoterpenes used in this study and possessing cyclohexene ring, i.e. *S*(–)-limonene and (–)-α-pinene, gave analogous oxidation reactions products.

Table 2. Epoxidation of styrene and cyclohexene in the presence of molybdenum(VI) Schiff base complexes as catalysts.

entry	catalyst	substrate	yield (%)	oxidant	epoxide (%)
1	**MoO_2L^2**	styrene	18	H_2O_2	74
2	**MoO_2L^4**	styrene	21	H_2O_2	81
3	**MoO_2L^7**	styrene	16	H_2O_2	79
4	**MoO_2L^1**	styrene	74	TBHP	81
5	**MoO_2L^2**	styrene	82	TBHP	88
6	**MoO_2L^3**	styrene	78	TBHP	83
7	**MoO_2L^4**	styrene	74	TBHP	80
8	**MoO_2L^5**	styrene	72	TBHP	85
9	**MoO_2L^6**	styrene	73	TBHP	83
10	**MoO_2L^7**	styrene	66	TBHP	80
11	**MoO_2L^2**	cyclohexene	19	H_2O_2	98
12	**MoO_2L^4**	cyclohexene	25	H_2O_2	98
13	**MoO_2L^7**	cyclohexene	22	H_2O_2	99
14	**MoO_2L^1**	cyclohexene	67	TBHP	99
15	**MoO_2L^2**	cyclohexene	77	TBHP	99
16	**MoO_2L^3**	cyclohexene	74	TBHP	98
17	**MoO_2L^4**	cyclohexene	71	TBHP	99
18	**MoO_2L^5**	cyclohexene	73	TBHP	99
19	**MoO_2L^6**	cyclohexene	71	TBHP	98
20	**MoO_2L^7**	cyclohexene	69	TBHP	99

Generally, cyclohexene and (–)-α-pinene were converted to their corresponding epoxides with roughly the same yields as in the case of styrene, but selectivities to their epoxides are clearly much higher, especially in the case of cyclohexene (Table 2, entries 11-20) with excellent up to 99% formation of cyclohexene oxide. In case of (–)-α-pinene and when TBHP was used the main product was (–)-α-pinene oxide (up to 89%), but with aqueous 30% H_2O_2, lower conversions were achieved and even over 30% of verbenol, allylic oxidation product, was formed (Table 3, entries 11-20).

Suprisingly, *S*(–)-limonene was oxidized selectively to its epoxide with excellent conversion, especially with TBHP (Table 3, entries 4-10), than in case of all the other substrates, i.e. styrene, cyclohexene and (–)-α-pinene. When TBHP was used as the terminal oxidant *cis*- and *trans*-1,2-limonene oxide are formed almost in equal proportions, provided epoxide practically quantitatively with and only small amounts of diepoxide, due to the presence of additional exocyclic isopropenyl moiety, as by-product were obtained. On the other hand, the epoxidation using aqueous 30% H_2O_2 resulted only in epoxide formation (Table 3, entries 1-3) but with an high excess of *trans*-1,2-limonene oxide.

Under the same reaction conditions, but at very low 0.05% loadings of two dioxidomolybdenum(VI) complexes equipped with naphtholate-oxazoline ligands as catalysts the oxidation of *R*(+)-limonene resulted in *ca.* 60% conversion and up to 64% selectivity towards epoxide [39]. On the other hand, Judmaier *et al.* [40] reported catalytic activity of dimeric μ-oxido bridged dioxidomolybdenum(VI) complex with reduced Schiff base, which

in chloroform at 50 °C show excellent epoxide yield and selectivity in the epoxidation of cyclohexene, but when *R*(+)-limonene was used as a substrate the reaction yielded in almost equal amounts of epoxide and diepoxide.

Figure 5. Possible epoxidation and allylic oxidation products of cyclohexene.

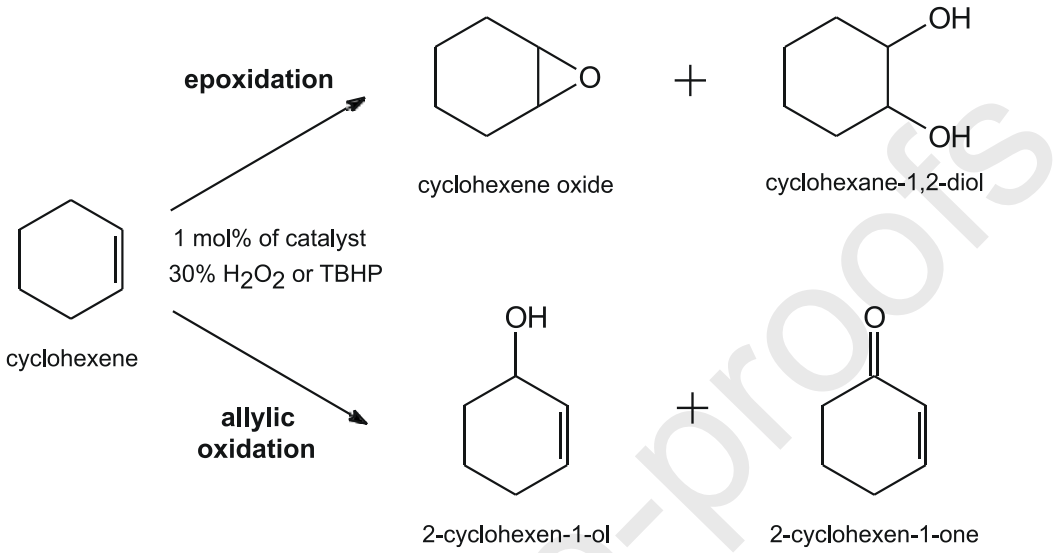


Table 3. Epoxidation of monoterpenes with catalytic amounts of molybdenum(VI) Schiff base complexes as catalysts.

entry	catalyst	substrate	yield (%)	oxidant	epoxide (%)
1	**MoO_2L^2**	*S*(–)-limonene	33	H_2O_2	83
2	**MoO_2L^4**	*S*(–)-limonene	37	H_2O_2	89
3	**MoO_2L^7**	*S*(–)-limonene	32	H_2O_2	85
4	**MoO_2L^1**	*S*(–)-limonene	96	TBHP	77
5	**MoO_2L^2**	*S*(–)-limonene	98	TBHP	82
6	**MoO_2L^3**	*S*(–)-limonene	99	TBHP	80
7	**MoO_2L^4**	*S*(–)-limonene	97	TBHP	74
8	**MoO_2L^5**	*S*(–)-limonene	99	TBHP	73
9	**MoO_2L^6**	*S*(–)-limonene	95	TBHP	76
10	**MoO_2L^7**	*S*(–)-limonene	97	TBHP	74
11	**MoO_2L^2**	(–)-α-pinene	14	H_2O_2	64
12	**MoO_2L^4**	(–)-α-pinene	18	H_2O_2	69
13	**MoO_2L^7**	(–)-α-pinene	17	H_2O_2	67
14	**MoO_2L^1**	(–)-α-pinene	67	TBHP	83
15	**MoO_2L^2**	(–)-α-pinene	74	TBHP	85
16	**MoO_2L^3**	(–)-α-pinene	72	TBHP	74
17	**MoO_2L^4**	(–)-α-pinene	68	TBHP	81
18	**MoO_2L^5**	(–)-α-pinene	65	TBHP	87
19	**MoO_2L^6**	(–)-α-pinene	62	TBHP	79
20	**MoO_2L^7**	(–)-α-pinene	75	TBHP	89

4. Conclusion

Within this paper we present the synthesis of ten new chiral *cis*-dioxidomolybdenum(VI) complexes derived from tetradentate Schiff bases, products of a single condensation of salicylaldehyde and its derivatives with *1S,2S*-(+)-2-amino-1-phenyl-1,3-propanediol, which have been characterized spectroscopically by UV-Vis, CD, IR, and NMR techniques.

All these complexes have proved catalytic activity in the asymmetric sulfoxidation of thioanisole by aqueous 30% H_2O_2 and *tert*-butyl hydroperoxide (TBHP) resulting in better yields and enantioselectivities when reactions were carried out in much lower temperatures. Furthermore, catalytic abilities of **MoO_2L^1-MoO_2L^7** complexes have been tested in the epoxidation of model olefinic substrates, i.e. styrene, cyclohexene and two monoterpenes, i.e. *S*(–)-limonene and (–)-α-pinene using the same terminal oxidants. These complexes are able to catalyze their oxidative conversion to corresponding epoxides with excellent yields and selectivities. Under optimized reaction conditions, the best results have been achieved for *S*(–)-limonene, which was oxidized selectively to its epoxide with excellent conversion using TBHP as the terminal oxidant. Formation of chiral limonene epoxide is especially important since its application as a key raw material in the synthesis of pharmaceuticals, fragrances, perfumes and food additives was proved. In the future we would like to concentrate our efforts on epoxidation of a number of chiral monoterpenes.

Acknowledgements

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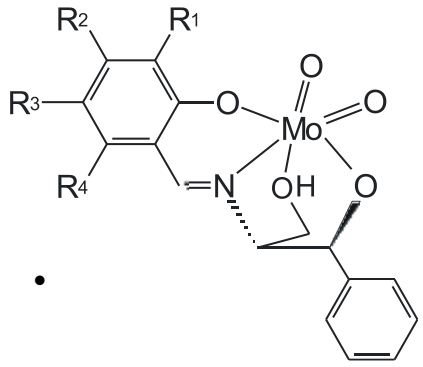

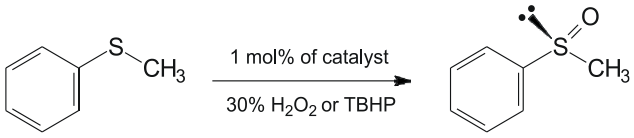

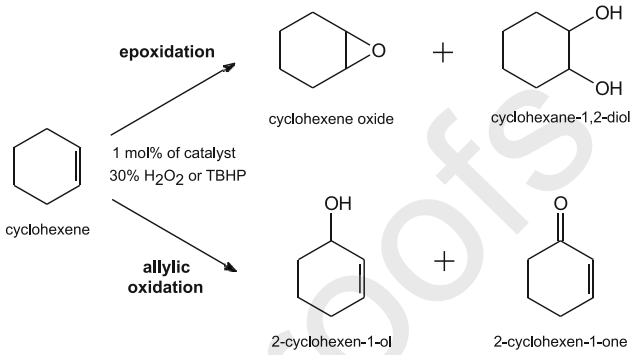

- Chiral *cis*-dioxidomolybdenum(VI) Schiff base complexes have been synthesized.
- The complexes were characterized by IR, CD, UV-Vis and NMR spectroscopy.
- The molybdenum(VI) complexes have ability to catalyze sulfoxidation of thioanisole.
- The complexes are also catalysts in the oxidation of alkenes and monoterpenes.

Marta Karman: Methodology, Investigation;
Grzegorz Romanowski: Conceptualization, Visualization, Writing - Original Draft, Writing - Reviewing and Editing.