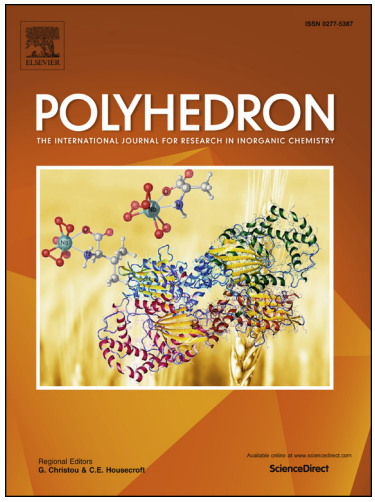

Synthesis, characterization and catalytic activity of dioxidomolybdenum(VI) complexes with tridentate Schiff bases derived from *1R,2S*(-)-norephedrine

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Synthesis, characterization and catalytic activity of dioxidomolybdenum(VI) complexes with tridentate Schiff bases derived from *1R,2S*(–)-norephedrine

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Abstract

New chiral dioxidomolybdenum(VI) complexes with tridentate Schiff base ligands obtained by monocondensation of *1R,2S*(–)-norephedrine with salicylaldehyde and its derivatives were synthesized. The complexes were characterized by elemental analysis and by their IR, CD, UV-Vis, one- (^{1}H) and two-dimensional (COSY, gHSQC and NOESY) NMR spectra. After optimization of reaction conditions, catalytic activity of these complexes were tested in the oxidation of olefins, *i.e.* styrene and cyclohexene, using aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as an oxidant. Moreover, the dioxidomolybdenum(VI) Schiff base complexes have also ability to catalyze the oxidation of thioanisole to methyl phenyl sulfoxide in presence of aqueous 30% H_2O_2.

1. Introduction

Molybdenum is a trace element, which is capable of forming complexes with many compounds of biological significance. It is also an important cofactor in the active site of many enzymes in plants and animals that catalyzes a number of diverse reactions. For plant growth, molybdenum is essential in the processes of atmospheric nitrogen fixation by convertion to ammonia (nitrogenases) and nitrate reduction to nitrite via nitrate reductase. In mammalian enzymes, it is part of a complex called molybdenum cofactor (Moco) required for xanthine oxidoreductase, xanthine dehydrogenase or xanthine oxidase that catalyzes oxidation of hypoxanthine to xanthine, xanthine to uric acid or participates in the metabolism of purines. Furthermore, sulfite oxidase is involved in the metabolism of sulfur-containing amino acids and finally, the last step of abscisic acid (ABA) biosynthesis involves oxidation of its aldehyde catalyzed by aldehyde oxidase [1,2].

Such enzymes can be modeled by molybdenum complexes with chiral N-salicyl-*β*-amino alcohol Schiff base ligands [3,4]. These "tridentate salen ligands" are very attractive due to their simple synthesis from naturally available chiral amino acids [5,6] and structural and electronic fine-tunability [7]. Many transition metal complexes, including these with Schiff bases and molybdenum(VI) or vanadium(V) cation have been successfully employed as catalysts in epoxidation of olefins [8], the asymmetric alkynylation of aldehydes [9], the stereoselective synthesis of cyclic ethers [10,11] and trimethylsilylcyanations [12] and oxidation of sulfides to sulfoxides [9,13,14]. Especially in case of enantioselective sulfoxidation, molybdenum complexes are much less successful and explored [15]. Until now, various systems have been developed successfully for the asymmetric sulfoxidation [16] and epoxidation reactions of alkenols [17] using in situ generated molybdenum and vanadium-based catalysts.

In continuation of our studies on synthesis, structure, spectroscopic and catalytic properties of transition metal complexes incorporating chiral tridentate Schiff base ligands [18-20], we prepared a series of new dioxidomolybdenum(VI) complexes with ONO donor

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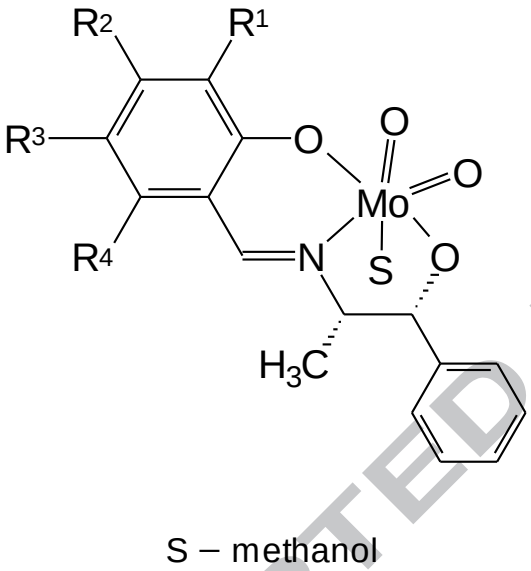
Schiff base ligands, products of monocondensation of *1R,2S*(–)-norephedrine with aromatic *o*-hydroxyaldehydes, presented in Fig. 1. Their spectroscopic properties by 1D and 2D NMR, UV-Vis, CD and IR have been examined. The catalytic potential of these complexes in the enantioselective sulfoxidation of thioanisole utilizing aqueous 30% H_2O_2 as an oxidant has been studied. Moreover, they were also used as catalysts in the oxidation of olefins, *i.e.* styrene and cyclohexene, in presence of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) in decane.

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



S – methanol

	R^1	R^2	R^3	R^4
1	H	H	H	H
2	OCH_3	H	H	H
3	H	H	OCH_3	H
4	H	OCH_3	H	OCH_3
5	H	H	CH_3	H
6	H	H	Br	H
7	H	H	NO_2	H
8	H	OH	H	H
9	$C(CH_3)_3$	H	$C(CH_3)_3$	H
10	H	H	$-(CH)_4-$	

2. Experimental

2.1. Measurements

All chemicals and reagents were obtained from commercial sources and used without further purification unless stated otherwise. Carbon, hydrogen and nitrogen contents were determined on a Carlo Erba MOD 1106 elemental analyzer. IR spectra of solid samples (KBr pellets) were run on a Bruker IFS 66 and electronic spectra on the Perkin-Elmer LAMBDA 18 spectrophotometer. Circular dichroism spectra were measured with a Jasco J-815 spectropolarimeter. 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 analyze the reaction products of the oxidation of olefins. The identity of the products was confirmed using a GC-MS model Shimadzu GCMS-QP2010 SE.

2.2. Catalytic activity

2.2.1. Sulfoxidation

In typical procedure, to a solution of catalyst (0.010 mmol) in 3 ml of CH_2Cl_2/MeOH mixture (7:3), thioanisole (1.00 mmol) was added at room temperature or –20 ^oC, together with 1,3,5-trimethoxybenzene as an internal standard. Aqueous 30% H_2O_2 was added (1.10 mmol) by small portions and the resulting mixture was stirred. After the appropriate reaction time, the solution was quenched with 3 ml of sodium sulphite solution (0.1 M) and extracted with ethyl acetate (3 × 3 ml). The combined organic layers were evaporated to dryness. The solid product dissolved in $CDCl_3$ was analyzed (yield and *ee* value) by ^1H NMR spectra in the presence of chiral shift reagent $Eu(hfc)_3$ (where Hhfc is 3-(heptafluoropropylhydroxymethylene)-(+)-camphoric acid) [21].

2.2.2. Oxidation of olefins

In typical procedure, styrene or cyclohexene (1.00 mmol), an oxidant (2.00 mmol), *i.e.* aqueous 30% H_2O_2 or 5.5 M *tert*-butyl hydroperoxide (TBHP) in decane, and catalyst (0.010 mmol) were heated at 80 ^oC for 1 h of reaction time in 10 ml of 1,2-dichloroethane (DCE). The reactions were monitored by GC and the yields were recorded as GC yield based on the starting styrene or cyclohexene. The identity of oxidation products were confirmed by GC-MS. The influence of amounts of catalyst and oxidant were also studied to check their effect on the conversion and selectivity of the reaction products.

2.3. Synthesis of dioxidomolybdenum(VI) complexes

The complexes were obtained in a following example procedure. A solution of 1 mmol of *1R,2S*(–)-norephedrine in absolute ethanol (10 ml) was added with stirring to 1 mmol of an aromatic *o*-hydroxyaldehyde (salicylaldehyde, 3-methoxysalicylaldehyde, 5-methoxysalicylaldehyde, 4,6-dimethoxysalicylaldehyde, 5-methylsalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, 4-hydroxysalicylaldehyde, 3,5-di-*tert*-butylsalicylaldehyde or 2-hydroxy-1-naphthaldehyde) in MeOH (10 ml) and heated under reflux for 1 h. Then, bis(acetylacetonato)dioxidomolybdenum(VI) (1 mmol) in MeOH (10 ml) was added and stirred at room temperature for 2 h. After cooling in a fridge a solid was separated and filtered off and washed several times with MeOH.

*2.3.1. {1R,2S(–)-2-[(1-oxido-1-phenylpropyl)iminomethyl]phenolato-κ^3N,O,O'}dioxidomolybdenum(VI) methanol solvate (**1**)*

Yield 85%. *Anal.* Calc. for $C_{16}H_{15}NO_4Mo{\cdot}CH_3OH$: C, 49.4; H, 4.6; N, 3.4. Found: C, 49.2; H, 4.6; N, 3.5%. IR (KBr, cm^{-1}): 1639 ($\nu_{C=N}$); 929, 900 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 275 (8240), 368 (2630). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 279 (-6.27), 301 (0.42), 364 (-5.68). ^1H NMR (DMSO-d_6, ppm): 8.69 (1H, s) (azomethine); 7.56 (1H, d, ^3J=7.7 Hz), 7.48 (1H, t, ^3J=7.7 Hz), 7.42-7.35 (4H, m), 7.30 (1H, t, ^3J=7.5 Hz), 6.96 (1H, t, ^3J=7.7 Hz), 6.85 (1H, d, ^3J=8.9 Hz) (aromatic); 5.56 (1H, d, ^3J=4.3 Hz), 4.53 (1H, m) (methine); 0.94 (1H, d, ^3J=6.9 Hz) (methyl); 4.10 (1H, q), 3.18 (3H, d, ^3J=5.2 Hz) (MeOH).

*2.3.2. {1R,2S(–)-2-[(1-oxido-1-phenylpropyl)iminomethyl]-6-methoxyphenolato-κ^3N,O,O'}dioxidomolybdenum(VI) methanol solvate (**2**)*

Yield 88%. *Anal.* Calc. for $C_{17}H_{17}NO_5Mo \cdot CH_3OH$: C, 48.8; H, 4.8; N, 3.2. Found: C, 48.7; H, 4.6; N, 3.1%. IR (KBr, cm^{-1}): 1631 ($\nu_{C=N}$); 1257 ($\nu_{asym(C-O)}$); 1034 ($\nu_{sym(C-O)}$); 927, 883 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 276 (7600), 376 (2590). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 282 (-5.46), 310 (0.72), 375 (-4.77). ^{1}H NMR (DMSO-d_6, ppm): 8.85 (1H, s) (azomethine); 7.46-7.41 (4H, m), 7.34 (1H, t, ^{3}J=7.5 Hz), 7.26 (1H, d, ^{3}J=7.9 Hz), 7.23 (1H, d, ^{3}J=7.9 Hz), 6.98 (1H, t, ^{3}J=7.9 Hz) (aromatic); 5.59 (1H, d, ^{3}J=4.3 Hz), 4.58 (1H, m) (methine); 3.72 (3H, s) (methoxy); 0.96 (1H, d, ^{3}J=6.8 Hz) (methyl); 4.10 (1H, q), 3.18 (3H, d, ^{3}J=5.2 Hz) (MeOH).

*2.3.3. {1R,2S(–)-2-[(1-oxido-1-phenylpropyl)iminomethyl]-4-methoxyphenolato-κ^3N,O,O'}dioxidomolybdenum(VI) methanol solvate (**3**)*

Yield 82%. *Anal.* Calc. for $C_{17}H_{17}NO_5Mo \cdot CH_3OH$: C, 48.8; H, 4.8; N, 3.2. Found: C, 48.6; H, 4.7; N, 3.2%. IR (KBr, cm^{-1}): 1636 ($\nu_{C=N}$); 1258 ($\nu_{asym(C-O)}$); 1029 ($\nu_{sym(C-O)}$); 928, 897 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 276 (7490), 373 (2540). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 281 (-5.11), 298 (0.20), 319 (-1.60), 384 (-4.57). ^{1}H NMR (DMSO-d_6, ppm): 8.77 (1H, s) (azomethine); 7.40-7.36 (4H, m), 7.28 (1H, t, ^{3}J=7.5 Hz), 7.18 (1H, d, ^{3}J=3.2 Hz), 7.15 (1H, dd, ^{3}J=9.0 Hz, ^{4}J=3.2 Hz), 6.88 (1H, d, ^{3}J=9.0 Hz) (aromatic); 5.53 (1H, d, ^{3}J=4.3 Hz), 4.50 (1H, m) (methine); 3.73 (3H, s) (methoxy); 0.91 (1H, d, ^{3}J=6.8 Hz) (methyl); 4.10 (1H, q), 3.18 (3H, d, ^{3}J=5.2 Hz) (MeOH).

*2.3.4. {1R,2S(–)-2-[(1-oxido-1-phenylpropyl)iminomethyl]-3,5-dimethoxyphenolato-κ^3N,O,O'}dioxidomolybdenum(VI) methanol solvate (**4**)*

Yield 78%. *Anal.* Calc. for $C_{18}H_{19}NO_6Mo \cdot CH_3OH$: C, 48.2; H, 4.9; N, 3.0. Found: C, 48.2; H, 5.0; N, 3.0%. IR (KBr, cm^{-1}): 1623 ($\nu_{C=N}$); 1256 ($\nu_{asym(C-O)}$); 1027 ($\nu_{sym(C-O)}$); 924, 894 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 306 (12700). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 264 (4.04), 299 (-5.84), 340 (-7.47). ^{1}H NMR (DMSO-d_6, ppm): 8.87 (1H, s) (azomethine); 7.39-7.34 (4H, m), 7.27 (1H, t, ^{3}J=7.5 Hz), 6.16 (1H, d, ^{3}J=2.2 Hz), 6.12 (1H, d, ^{3}J=2.2 Hz) (aromatic); 5.52 (1H, d, ^{3}J=4.3 Hz), 4.52 (1H, m) (methine); 3.86 (3H, s), 3.81 (3H, s) (methoxy); 0.87 (1H, d, ^{3}J=6.8 Hz) (methyl); 4.10 (1H, q), 3.18 (3H, d, ^{3}J=5.2 Hz) (MeOH).

*2.3.5. {1R,2S(–)-2-[(1-oxido-1-phenylpropyl)iminomethyl]-4-methylphenolato-κ^3N,O,O'}dioxidomolybdenum(VI) methanol solvate (**5**)*

Yield 77%. *Anal.* Calc. for $C_{17}H_{17}NO_4Mo \cdot CH_3OH$: C, 50.6; H, 5.0; N, 3.3. Found: C, 50.5; H, 5.1; N, 3.2%. IR (KBr, cm^{-1}): 1632 ($\nu_{C=N}$); 919, 890 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 275 (9310), 364 (2120). CD spectrum in DMSO [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 281 (-7.88), 300 (0.18), 363 (-6.22). ^{1}H NMR (DMSO-d_6, ppm): 8.73 (1H, s) (azomethine); 7.40-7.36 (5H, m), 7.33 (1H, dd, ^{3}J=8.4 Hz, ^{4}J=2.2 Hz), 7.28 (1H, t, ^{3}J=9.7 Hz), 6.84 (1H, d, ^{3}J=8.4 Hz) (aromatic); 5.54 (1H, d, ^{3}J=4.3 Hz), 4.51 (1H, m) (methine); 2.29 (3H, s), 0.90 (1H, d, ^{3}J=6.8 Hz) (methyl); 4.10 (1H, q), 3.18 (3H, d, ^{3}J=5.2 Hz) (MeOH).

*2.3.6. {1R,2S(–)-2-[(1-oxido-1-phenylpropyl)iminomethyl]-4-bromophenolato-κ^3N,O,O'}dioxidomolybdenum(VI) methanol solvate (**6**)*

Yield 82%. *Anal.* Calc. for $BrC_{16}H_{14}NO_4Mo \cdot CH_3OH$: C, 41.5; H, 3.7; N, 2.9. Found: C, 41.4; H, 3.8; N, 3.0%. IR (KBr, cm^{-1}): 1634 ($\nu_{C=N}$); 924, 895 ($\nu_{Mo=O}$). UV-Vis spectrum in

DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 277 (9380), 366 (2260). CD spectrum in DMSO [λ_{max} (nm), Δε (M^{-1} cm^{-1})]: 285 (-7.25), 304 (0.11), 366 (-5.79). ^{1}H NMR (DMSO-d_6, ppm): 8.74 (1H, s) (azomethine); 7.75 (1H, s), 7.61 (1H, dd, ^{3}J=8.4 Hz, ^{4}J=2.2 Hz), 7.44-7.37 (5H, m), 6.93 (1H, d, ^{3}J=8.4 Hz) (aromatic); 5.54 (1H, d, ^{3}J=4.3 Hz), 4.51 (1H, m) (methine); 0.92 (1H, d, ^{3}J=6.8 Hz) (methyl); 4.10 (1H, q), 3.18 (3H, d, ^{3}J=5.2 Hz) (MeOH).

*2.3.7. {1R,2S(–)-2-[(1-oxido-1-phenylpropyl)iminomethyl]-4-nitrophenolato-κ^3N,O,O'}dioxidomolybdenum(VI) methanol solvate (**7**)*

Yield 79%. *Anal.* Calc. for $C_{16}H_{14}N_2O_6Mo\cdot CH_3OH$: C, 44.6; H, 4.0; N, 6.1. Found: C, 44.5; H, 3.9; N, 6.2%. IR (KBr, cm^{-1}): 1648 ($\nu_{C=N}$); 929, 907 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 344 (14800). CD spectrum in DMSO [λ_{max} (nm), Δε (M^{-1} cm^{-1})]: 258 (-7.11), 298 (0.84), 328 (-4.48). ^{1}H NMR (DMSO-d_6, ppm): 9.04 (1H, s) (azomethine); 8.68 (1H, d, ^{3}J=3.0 Hz), 8.38 (1H, dd, ^{3}J=9.2 Hz, ^{4}J=3.0 Hz), 7.47-7.31 (4H, m), 7.36 (1H, t, ^{3}J=8.8 Hz), 7.15 (1H, d, ^{3}J=9.2 Hz) (aromatic); 5.73 (1H, d, ^{3}J=4.3 Hz), 4.65 (1H, m) (methine); 1.01 (1H, d, ^{3}J=7.0 Hz) (methyl); 4.16 (1H, q), 3.23 (3H, s) (MeOH).

*2.3.8. {1R,2S(–)-2-[(1-oxido-1-phenylpropyl)iminomethyl]-5-hydroxyphenolato-κ^3N,O,O'}dioxidomolybdenum(VI) methanol solvate (**8**)*

Yield 82%. *Anal.* Calc. for $C_{16}H_{15}NO_5Mo\cdot CH_3OH$: C, 47.6; H, 4.5; N, 3.3. Found: C, 47.4; H, 4.4; N, 3.3%. IR (KBr, cm^{-1}): 1632 ($\nu_{C=N}$); 931, 893 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 288 (7410), 343 (2210). CD spectrum in DMSO [λ_{max} (nm), Δε (M^{-1} cm^{-1})]: 263 (5.16), 294 (-8.47), 346 (-7.18). ^{1}H NMR (DMSO-d_6, ppm): 10.32 (1H, s) (hydroxyl); 8.59 (1H, s) (azomethine); 7.40-7.34 (5H, m), 7.27 (1H, t, ^{3}J=7.5 Hz), 8.43 (1H, d, ^{3}J=8.4 Hz), 6.27 (1H, s) (aromatic); 5.53 (1H, d, ^{3}J=4.3 Hz), 4.44 (1H, m) (methine); 0.88 (1H, d, ^{3}J=6.9 Hz) (methyl); 4.10 (1H, q), 3.17 (3H, d, ^{3}J=5.2 Hz) (MeOH).

*2.3.9. {1R,2S(–)-2-[(1-oxido-1-phenylpropyl)iminomethyl]-4,6-di-tert-butylphenolato-κ^3N,O,O'}dioxidomolybdenum(VI) methanol solvate (**9**)*

Yield 75%. *Anal.* Calc. for $C_{24}H_{31}NO_4Mo\cdot CH_3OH$: C, 57.1; H, 6.7; N, 2.7. Found: C, 57.1; H, 6.6; N, 2.8%. IR (KBr, cm^{-1}): 1632 ($\nu_{C=N}$); 920, 891 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 280 (7780), 363 (1600). CD spectrum in DMSO [λ_{max} (nm), Δε (M^{-1} cm^{-1})]: 284 (-7.95), 304 (0.13), 369 (-6.19). ^{1}H NMR (DMSO-d_6, ppm): 8.79 (1H, s) (azomethine); 7.50 (1H, d, ^{3}J=2.3 Hz), 7.34 (1H, d, ^{3}J=2.3 Hz) 7.40-7.36 (4H, m), 7.28 (1H, t, ^{3}J=9.3 Hz) (aromatic); 5.54 (1H, d, ^{3}J=4.3 Hz), 4.44 (1H, m) (methine); 1.40 (9H, s), 1.30 (9H, s) (*tert*-butyl); 0.92 (1H, d, ^{3}J=6.9 Hz) (methyl); 4.11 (1H, q), 3.18 (3H, d, ^{3}J=5.2 Hz) (MeOH).

*2.3.10. {1R,2S(–)-2-[(1-oxido-1-phenylpropyl)iminomethyl]naphtholato-κ^3N,O,O'}dioxidomolybdenum(VI) methanol solvate (**10**)*

Yield 77%. *Anal.* Calc. for $C_{20}H_{17}NO_4Mo\cdot CH_3OH$: C, 54.4; H, 4.6; N, 3.0. Found: C, 54.2; H, 4.5; N, 3.1%. IR (KBr, cm^{-1}): 1623 ($\nu_{C=N}$); 932, 902 ($\nu_{Mo=O}$). UV-Vis spectrum in DMSO [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 273 (8860), 308 (11230), 382 (4060). CD spectrum in DMSO [λ_{max} (nm), Δε (M^{-1} cm^{-1})]: 283 (-2.04), 306 (-5.05), 379 (-6.45). ^{1}H NMR (DMSO-d_6, ppm): 8.68 (1H, s) (azomethine); 8.29 (1H, d, ^{3}J=9.1 Hz), 8.01 (1H, d, ^{3}J=9.1 Hz), 7.80 (1H, d, ^{3}J=9.1 Hz), 7.60-7.55 (4H, m), 7.53 (1H, t, ^{3}J=9.1 Hz), 7.45 (1H, t, ^{3}J=9.3 Hz), 7.40 (1H, t,

^{3}J=9.1 Hz), 7.18 (1H, d, ^{3}J=9.1 Hz) (aromatic); 5.56 (1H, d, ^{3}J=4.3 Hz), 4.47 (1H, m) (methine); 0.95 (1H, d, ^{3}J=6.9 Hz) (methyl); 4.10 (1H, q), 3.17 (3H, d, ^{3}J=5.2 Hz) (MeOH).

3. Results and discussion

3.1. Spectroscopic properties

The electronic, circular dichroism, ^{1}H NMR and selected solid-state IR spectral data are listed in Section 2.

The IR spectra of solid complexes display strong C=N stretch (at 1623-1648 cm^{-1}) which may be assigned the azomethine group of Schiff base ligands coordinated to dioxidomolybdenum(VI) moiety [22]. In case of compounds **2**, **3** and **4**, with methoxy substituents attached to aromatic ring of salicyl moiety, asymmetric and symmetric C-O stretches have been found at *ca.* 1260 and 1030 cm^{-1}, respectively. In addition, the molybdenum(VI) complexes display two sharp bands at 919-932 and 883-907 cm^{-1} due to the ν_{asym}(O=Mo=O) and ν_{sym}(O=Mo=O) modes, respectively, which indicate the presence of a *cis*-[$Mo^{VI}O_2$] structure [23].

The electronic and circular dichroism spectra of all complexes were recorded in DMSO. Strong intense bands, ε_{max} = 7410-9380 $dm^3mol^{-1}cm^{-1}$, with λ_{max} in region 273-288 nm are considered to arise from intraligand π-π^* transitions. The low energy bands, recorded for all complexes, between 343-382 nm (ε_{max} = 1600-4060 $dm^3mol^{-1}cm^{-1}$) may be assigned as a ligand-to-metal charge transfer (LMCT) transition originating from the p_π orbital on the phenolate oxygen to the empty d orbital of molybdenum atom [24]. The spectrum of **10**, examined in the same region, display additional band at 308 nm (ε_{max} = 11200). In the case of compounds **4** and **7**, there are only single intense bands at around 306 (ε_{max} = 12700) and 344 nm (ε_{max} = 14 800), similar to vanadium(V) complex with the same chiral Schiff base ligand, with bands at 316 and 348 nm, respectively [19].

The circular dichroism spectra of **1**-**3**, **5**-**7** and **9** revealed the same bands in the 258-285 nm and the 328-384 nm range of the same origin as electronic spectra with a very strong negative sign of the Cotton effects and additional one with a positive sign of the Cotton effects at the 294-310 nm range. Moreover, there are two exceptions, **4** and **8**, which show bands with a strong positive sign of the Cotton effects at 264 and 263 nm and with a very strong negative sign of the Cotton effects at 299 and 294 nm, respectively. Furthermore, complex **10** derived from 2-hydroxy-1-naphthaldehyde, displays three strong bands with a negative sign of the Cotton effects at 283, 306 and 379 nm.

The one- (^{1}H) and two-dimensional (COSY, gHSQC and NOESY) NMR spectra of all the molybdenum(VI) complexes were recorded in DMSO-d_6. The signals were assigned on the basis of intensity, spin-spin coupling pattern and chemical shifts. Single condensation of salicylaldehyde and its derivatives with *1R*,*2S*(–)-norephedrine is confirmed by the presence of azomethine proton signals in the ^{1}H NMR spectra of all **1**-**10** complexes, similar as reported earlier for the vanadium(V) complexes derived from the same chiral Schiff base ligand [19]. Two-dimensional NMR experiments allow to unambiguously identify all protons and carbon atoms and establish connection and proximity between all protons and their attachment to carbon atoms, what we further discuss on the example of complex **3**. For example, its COSY spectrum shows cross-peaks between methine proton signal at 4.50 ppm and second methine proton doublet at 5.53 ppm, and also with methyl proton doublet at 0.91 ppm. In aromatic parts of the ligand, there are cross-peaks between 7.40-7.36 ppm multiplet and triplet at 7.28 ppm (protons of phenyl group in norephedrine fragment) and between doublet at 6.88 ppm and doublet of doublets at 7.15 ppm (salicylidene fragment). Moreover, NOESY spectra exhibit cross-peaks between the signal of the azomethine proton at 8.77 ppm

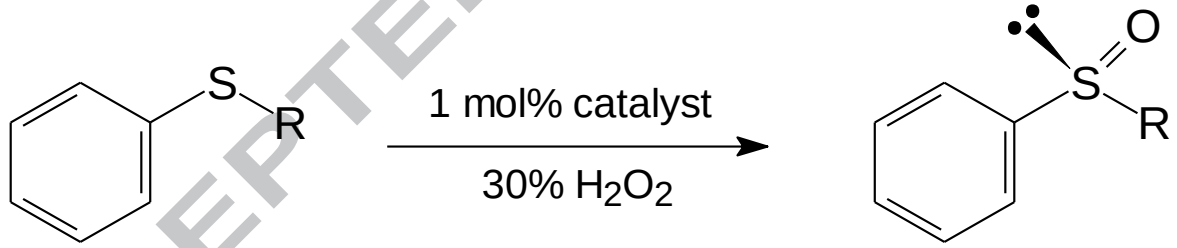
and methine proton signal at 4.50 ppm, also with doublet of methyl protons at 0.91 ppm and with salicylidene aromatic proton doublet at 7.18 ppm. The latter aromatic proton (7.18 ppm) also show cross-peak with signal of methoxy substituent protons at 3.73 ppm. As expected, there is no corresponding cross-peak between the signals of the azomethine proton at 8.77 ppm and the methine proton at 5.53 ppm. The coordination of a methanol molecule to the all molybdenum atoms of these complexes was confirmed by appearance of signals at around 3.18 and 4.10 ppm.

3.2. Catalytic activity studies

3.2.1. Sulfoxidation

The dioxidomolybdenum(VI) complexes **1**-**10** have been tested for their ability to catalyze the oxidation of prochiral sulfides using methyl phenyl sulfide (thioanisole) as model substrate with the optimized reaction conditions (Fig. 2). In this purpose, aqueous 30% H_2O_2 was used as an oxidant in a slight excess of 1.10 equivalents based on the sulfide substrate and reactions were run with 1 mol% of catalyst based on the model substrate in a mixture of CH_2Cl_2 and CH_3OH (7:3). With dichloromethane the best enantioselectivities were achieved, but methanol was necessary for a better mixing of the aqueous oxidant with the halogenated solvent [25,26]. Moreover, protic solvents can significantly enhance yield and selectivity of sulfoxide [27]. The results of catalytic studies are listed in Table 1.

Figure 2. Sulfoxidation of thioanisole catalyzed by dioxidomolybdenum(VI) complexes.



The best results have been obtained at room temperature for complexes **2**-**5** and **8** as catalysts (Table 1, entries 2-5 and 8). An overall yields for all catalysts were in the range of 77-89% within 45 min reaction time and enantiomeric excesses (ee's) with up to 28% for the *S*-configured sulfoxide were obtained. With the reaction carried out at –20 ^{o}C for **2**-**5** and **8** as catalysts in the oxidation of thioanisole, enantioselectivities improve significantly to 32-37% and a conversion up to 91% is observed after 210 min of the reaction time (Table 1, entries 11-15). In addition it is noteworthy that under the given conditions no over oxidation to the sulfone could be observed.

Generally, the best results have been obtained in the oxidation of thioanisole with catalysts possessing electron donating groups. The best enantioselectivities for **2**-**5** and **8** as compared to other catalysts may be result of a higher electron density on the phenolate oxygen, *e.g.* due to the highest electron-donating resonance effect contributing to an attainment of sufficient nucleophilicity by the metal centre. Mimoun *et al.* [28] pointed out

the importance of sufficiently nucleophilic centre for the oxidative catalysis of organic substrates.

Table 1. Catalytic oxidation of thioanisole by aqueous 30% H_2O_2 in presence of 1 mol% molybdenum(VI) Schiff base complexes as catalysts.

Entry	Catalyst	Yield (%)	*T* (^oC)	*t* (min)	*ee* (%) [a]
1	**1**	89	rt	45	20
2	**2**	87	rt	45	27
3	**3**	84	rt	45	24
4	**4**	81	rt	45	25
5	**5**	83	rt	45	23
6	**6**	79	rt	45	21
7	**7**	77	rt	45	18
8	**8**	86	rt	45	28
9	**9**	82	rt	45	19
10	**10**	87	rt	45	21
11	**2**	84	-20	210	33
12	**3**	89	-20	210	37
13	**4**	91	-20	210	35
14	**5**	88	-20	210	30
15	**8**	91	-20	210	32

[a] All sulfoxides are in *S* configuration.

3.2.2. Oxidation of styrene

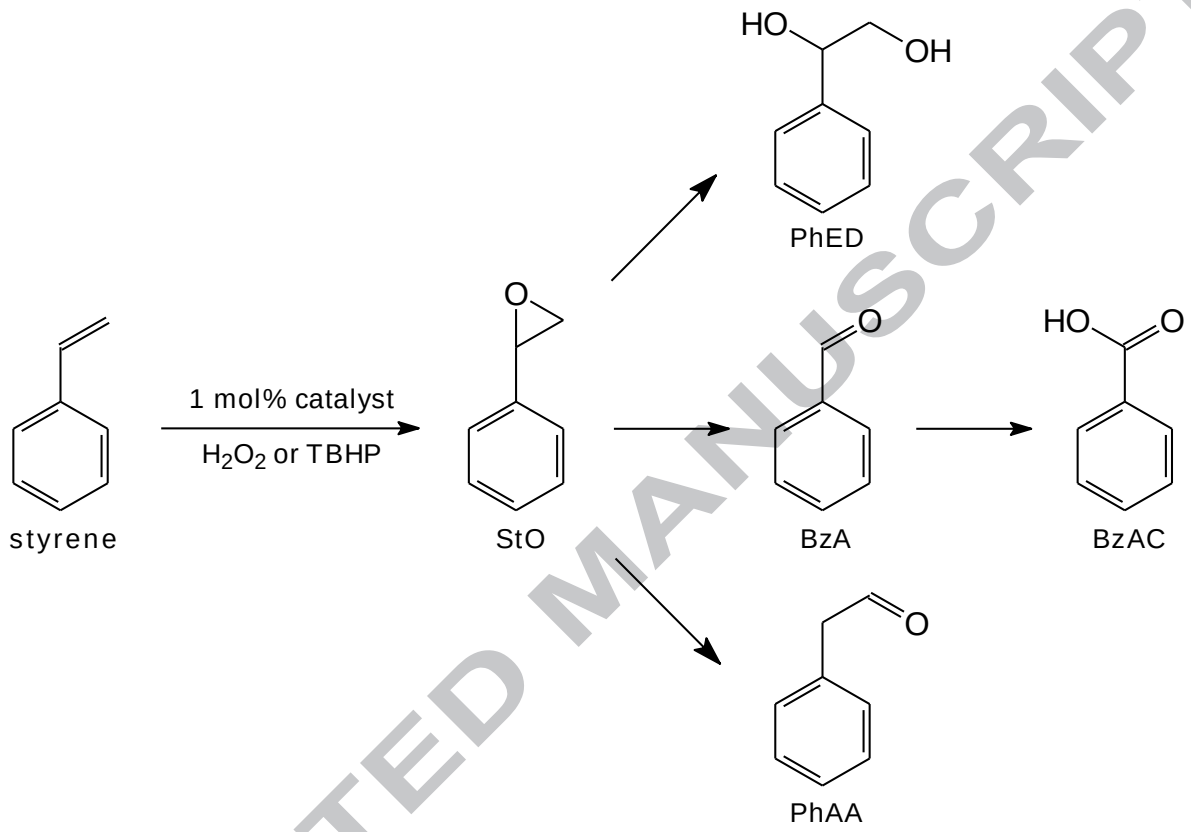
The oxidation of styrene with the **1-10** complexes as catalysts in 1,2-dichloroethane was performed in presence of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as an oxidant. In these reaction conditions styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde were obtained as the oxidation products (Fig. 3). The formation of all these products, conversion and selectivity are presented in Table 2.

In order to achieve suitable reaction conditions for a maximum oxidative conversion of styrene, complex **3** was taken as a representative catalyst and different parameters, *i.e.* amount of catalyst (0.5, 1 and 2 mol%) and an oxidant (in 1:1, 2:1 and 3:1 molar ratios to styrene), different solvents and temperatures of the reaction mixture were tested. Considering the highest conversion and reaction rate we found 1,2-dichloroethane (DCE) as the best solvent during our examination of olefins oxidation in different solvents such as methanol, ethanol, acetonitrile, chloroform, methylene chloride and 1,2-dichloroethane [24,29]. Moreover, as reported earlier [30], it was concluded that the higher reactions temperature can be also responsible for obtaining better yields and reaction rates.

To study the effect of amount of an oxidant, three different molar ratios of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) to styrene, *i.e.* 1:1, 2:1 and 3:1, styrene (1.00 mmol) and catalyst (0.010 mmol) were taken in DCE (10 ml), and the reaction was carried out for 1 h of contact time at 80 °C. At 1:1 molar ratio of H_2O_2 to styrene, a maximum of 29% conversion was achieved. Increasing the molar ratio to 2:1 improved the conversion to 51%, while 3:1 ratio has shown a maximum of 54% conversion. Further increment of 30% H_2O_2 shows no improvement in conversion. In case of using TBHP as an oxidant, increasing the TBHP:styrene ratio from 1:1, 2:1 to 3:1 improved the conversion from 43 to 72 and 74%,

respectively. As in the previous case the oxidation improved only marginally upon further addition of TBHP, therefore in both cases a 2:1 molar ratio being considered adequate.

Figure 3. Various products of catalytic oxidation of styrene.



Furthermore, three different amounts of **3** catalyst (0.5, 1 and 2 mol% in respect to substrate) with oxidant to styrene molar ratio of 2:1 under above reaction conditions were optimized. In this study, addition of 0.5 mol% gave only 19% (for 30% H_2O_2) and 34% (for TBHP) conversion, while 1 and 2 mol% have shown the conversion results as 51 and 72% for H_2O_2 and TBHP, respectively, for 1 h of reaction time. Upon further increasing of catalyst to 2 mol% reactions improved only marginally, which suggested that a higher amount of catalyst does not improve the oxidative conversion of styrene. Thus, 1 mol% of catalyst may be considered sufficient enough to run the reaction under above conditions. A blank reaction under the above reaction conditions gave with both oxidants *ca.* 2-5% conversion. Table 2 summarizes the percentage conversion of styrene and the selectivities for the various reaction products.

Using *tert*-butyl hydroperoxide (TBHP) in decane as an oxidant, under the optimized reaction conditions, *i.e.* 1.00 mmol of styrene, 2.00 mmol of oxidant, 1 mol% of catalyst and DCE as a solvent, all the complexes gave significantly higher 62-73% conversion (Table 2, entries 11-20), in comparison to the other reported earlier dioxidomolybdenum(VI) complex with Schiff base derived from 2-[(1-hydroxy-2-methylpropane-2-ylimino)methyl]naphthol, which gave 50% conversion, but with less excess of the oxidant and only 0.1 mol% of the catalyst [30]. The conversion results were very similar to, reported by us earlier [18], dioxidomolybdenum(VI) Schiff base complexes derived from *S*(+)-1-amino-2-propanol. Selectivity, in case of **1**-**10** catalysts, is rather similar and they are generally distinctly more

selective toward styrene oxide (59-71%) than benzaldehyde (20-34%). Furthermore, their selectivity against benzoic acid (2-4%), phenylacetaldehyde (2-4%) and 1-phenylethane-1,2-diol (1-2%) is relatively low. Judmaier *et al.* [23] described new dioxidomolybdenum(VI) Schiff base complexes with pendant OMe donor arms where two ligands coordinate in a bidentate manner to the metal center, which were used as catalysts in similar reactions but in chloroform at 50 ^{o}C. After 24 h, 71-75% conversion has been obtained in 5 h of reaction time with 97-98% of styrene oxide selectivity. When the dimeric dioxidomolybdenum(VI) complexes with one Schiff base in a tridentate manner were used as catalysts in the same reaction conditions only 35% conversion of styrene after 5 h and 44% conversion after 24 h have been achieved [31]. Moreover, in styrene oxidation with presence of dioxidomolybdenum(VI) catalysts derived from naphtholate-oxazoline ligands used at 0.05 mol% loadings in DCE at 80 ^{o}C and TBHP as an oxidant after 6 h of reaction time, the 76-83% conversion with very high selectivity to styrene oxide (90-92%) has been reported [32].

Table 2. Catalytic oxidation of styrene in presence of 1 mol% molybdenum(VI) Schiff base complexes in DCE.

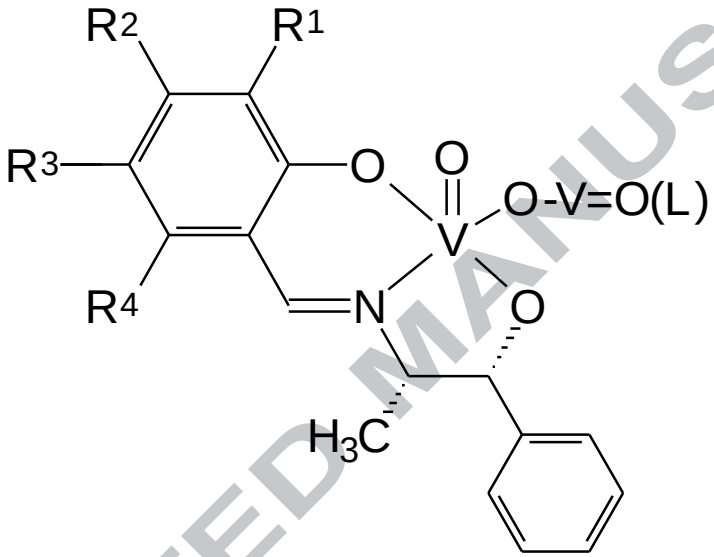
Entry	Catalyst	Oxidant	Conv. (%)	Product selectivity (%) [a]				
				StO	BzA	BzAC	PhAA	PhED
1	**1**	H_2O_2	44	38	57	-	-	5
2	**2**	H_2O_2	48	44	53	-	-	3
3	**3**	H_2O_2	51	46	50	-	-	4
4	**4**	H_2O_2	50	44	51	-	-	5
5	**5**	H_2O_2	43	42	52	-	-	6
6	**6**	H_2O_2	47	35	59	-	-	6
7	**7**	H_2O_2	41	32	64	-	-	4
8	**8**	H_2O_2	52	39	55	-	-	6
9	**9**	H_2O_2	48	45	50	-	-	5
10	**10**	H_2O_2	49	44	51	-	-	5
11	**1**	TBHP	63	66	27	2	3	2
12	**2**	TBHP	67	61	31	4	2	2
13	**3**	TBHP	72	65	27	3	3	2
14	**4**	TBHP	70	67	26	3	3	1
15	**5**	TBHP	73	71	20	2	4	1
16	**6**	TBHP	67	68	25	3	2	2
17	**7**	TBHP	62	59	34	3	3	1
18	**8**	TBHP	73	67	27	2	2	2
19	**9**	TBHP	68	64	29	2	4	1
20	**10**	TBHP	60	62	32	3	2	1

[a] StO – styrene oxide, BzA – benzaldehyde, BzAC – benzoic acid, PhAA – phenylacetaldehyde, PhED – 1-phenylethane-1,2-diol.

When catalytic oxidation of styrene in the same reaction conditions were performed, but with aqueous 30% H_2O_2 as an oxidizing agent, distinctly lower 41-52% conversion was found (Table 2, entries 1-10). Moreover, much lower selectivity against styrene oxide has been observed (32-46%) than in the case of TBHP. Moreover, all catalysts are much more selective toward benzaldehyde (50-64%) and slightly more selective toward 1-phenylethane-1,2-diol (3-6%).

Styrene oxide formed by epoxidation in the first step is very fast converted into benzaldehyde via nucleophilic attack of H_2O_2 to styrene oxide followed by the cleavage of the intermediate hydroperoxystyrene [33]. Benzaldehyde formation may also be facilitated by direct oxidative cleavage of the styrene side-chain double bond via a radical mechanism. Low conversion of styrene is probably caused by presence of significant amount of water in 30% H_2O_2, which can be responsible for the decomposition of catalyst and also the hydrolysis of styrene oxide to form 1-phenylethane-1,2-diol. Formation of other products, *e.g.* phenylacetaldehyde through isomerization of styrene oxide and benzoic acid through oxidation of benzaldehyde, are distinctly much slower processes.

Figure 4. Vanadium(V) Schiff base complexes derived from *1R,2S*(–)-norephedrine.



11: $R^1=R^2=R^3=R^4=H$
12: $R^2=R^3=R^4=H$, $R^1=OCH_3$
13: $R^1=R^2=R^4=H$, $R^3=OCH_3$
14: $R^1=R^3=H$, $R^2=R^4=OCH_3$
15: $R^1=R^2=R^4=H$, $R^3=CH_3$
16: $R^1=R^2=R^4=H$, $R^3=Br$
17: $R^1=R^2=H$, $R^3=NO_2$
18: $R^1=R^3=R^4=H$, $R^2=OH$
19: $R^2=R^3=R^4=H$, $R^1=C(CH_3)_3$
20: $R^1=R^2=H$, R^3-C_4H_4-R^4

For comparison to so far mentioned molybdenum(VI) catalysts (**1-10)**, oxidovanadium(V) complexes (Fig. 4) with the same chiral tridentate Schiff base ligands, **11-20**, have been also tested as catalysts in the oxidation of styrene, employing the same oxidants and using optimized amounts of catalysts (1 mol%), reaction time (6 h), oxidant to styrene molar ratio (3:1), temperature (80 °C) and solvent (acetonitrile). Synthesis, structure, spectroscopic characterization and catalytic properties in asymmetric sulfoxidation of these compounds have been reported by us earlier [19]. Using TBHP as an oxidant (Table 3, entries 11-20), conversion is quite similar (65-76%), as in the cases of molybdenum(VI) complexes, but much better than in case of the other dioxidovanadium(V) complexes (20-35% conversion) reported earlier [34]. On the other hand, the selectivity toward styrene oxide is considerably lower (52-63%). When aqueous 30% H_2O_2 is employed as an oxidant, distinctly much lower conversion of styrene has been observed (27-36%). Moreover, in comparison to

1-10, the selectivity much more differ (Table 3, entries 1-10) and, surprisingly, benzaldehyde is the main product (78–83%). Moreover, as well as for reported earlier dioxidovanadium(V) complexes [34], styrene oxide is the most expected product but its selectivity goes down considerably (>16%).

Table 3. Catalytic oxidation of styrene by in presence of 1 mol% vanadium(V) Schiff base complexes in acetonitrile.

Entry	Catalyst	Oxidant	Conv. (%)	Product selectivity (%)				
				StO	BzA	BzAC	PhAA	PhED
1	**11**	H_2O_2	31	13	81	-	-	6
2	**12**	H_2O_2	36	14	79	-	-	7
3	**13**	H_2O_2	34	16	80	-	-	4
4	**14**	H_2O_2	32	13	82	-	-	5
5	**15**	H_2O_2	27	14	81	-	-	5
6	**16**	H_2O_2	28	15	79	-	-	6
7	**17**	H_2O_2	31	12	79	-	-	9
8	**18**	H_2O_2	34	13	82	-	-	5
9	**19**	H_2O_2	35	14	78	-	-	8
10	**20**	H_2O_2	30	13	83	-	-	4
11	**11**	TBHP	74	55	39	4	2	-
12	**12**	TBHP	76	63	27	6	4	-
13	**13**	TBHP	70	61	32	4	3	-
14	**14**	TBHP	68	58	35	4	3	-
15	**15**	TBHP	73	57	34	5	4	-
16	**16**	TBHP	67	53	40	5	2	-
17	**17**	TBHP	65	52	39	6	3	-
18	**18**	TBHP	72	62	29	5	4	-
19	**19**	TBHP	70	57	37	4	2	-
20	**20**	TBHP	73	55	38	4	3	-

3.2.3. Oxidation of cyclohexene

The catalytic potential of the **1-10** complexes has been also found for the oxidation of cyclohexene in presence of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) in decane as an oxidant to give cyclohexene oxide, cyclohexane-1,2-diol, 2-cyclohexene-1-ol and 2-cyclohexene-1-one (Fig. 5). The formation of all these products, conversion and selectivity are presented in Table 4.

As in the case of the oxidation of styrene, complex **3** was taken as a representative catalyst for optimizing reaction conditions. In this purpose, the same amounts of catalyst (0.5, 1 and 2 mol%) and the oxidants (1:1, 2:1 and 3:1 molar ratios to cyclohexene) were tested. Different solvents and temperatures of the reaction mixture were also tested and, as earlier, the best results were found with 1,2-dichloroethane (DCE) as a solvent and at 80 °C.

Three different molar ratios of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) to cyclohexene, *i.e.* 1:1, 2:1 and 3:1 have been studied. Cyclohexene (1.00 mmol) and catalyst (0.010 mmol) were taken in DCE (10 ml), and the reaction was carried out for 1 h of contact time at 80 °C. At a H_2O_2 to cyclohexene 1:1 molar ratio, a maximum of 32% conversion was achieved. Increasing the ratio to 2:1 improved the conversion to 68%, while 3:1 ratio has shown a maximum of 69% conversion. Further increment of H_2O_2 shows no improved

conversion only marginally, therefore a 2:1 ratio being considered adequate. In case of using TBHP as an oxidizing agent, increasing the TBHP:cyclohexene molar ratio from 1:1 to 2:1 and 3:1 improved the conversion from 38 to 89 and 90%, respectively. As in the previous case, there was no significant conversion improvement upon further addition of any oxidant.

Figure 5. Various products of catalytic oxidation of cyclohexene.

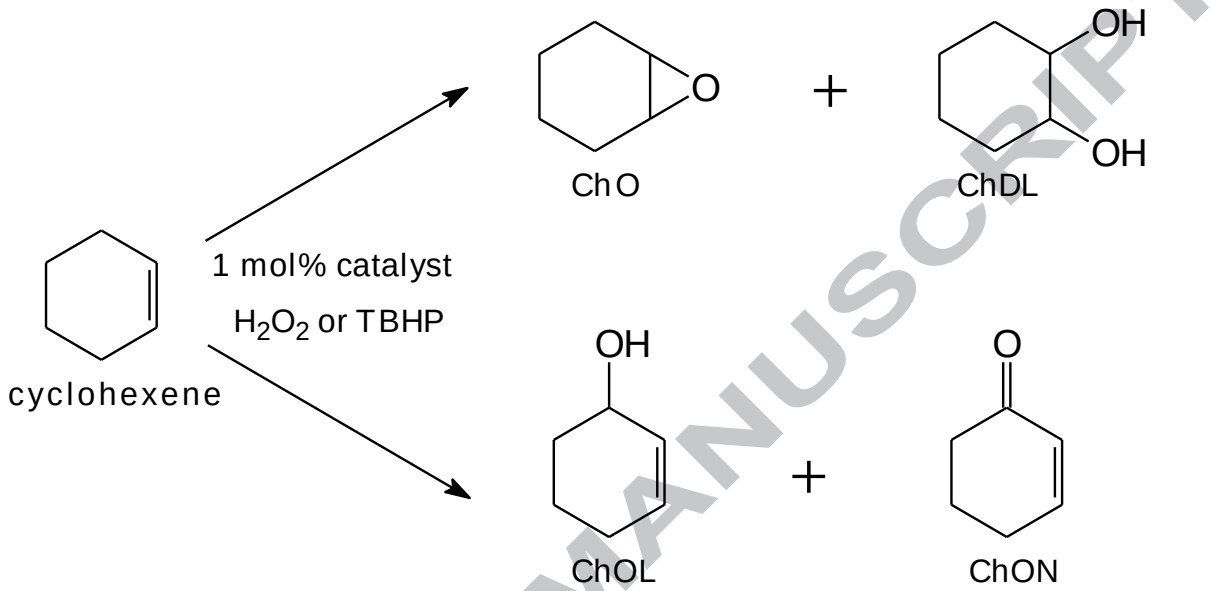


Table 4. Catalytic oxidation of cyclohexene in presence of 1 mol% molybdenum(VI) Schiff base complexes in DCE.

Entry	Catalyst	Oxidant	Conv. (%)	Product selectivity (%) [a]			
				ChO	ChOL	ChON	ChDL
1	**1**	H_2O_2	62	11	54	29	6
2	**2**	H_2O_2	70	13	61	22	4
3	**3**	H_2O_2	68	9	66	20	5
4	**4**	H_2O_2	67	10	62	21	7
5	**5**	H_2O_2	61	11	58	27	4
6	**6**	H_2O_2	63	10	64	21	5
7	**7**	H_2O_2	61	9	59	26	6
8	**8**	H_2O_2	69	10	62	25	3
9	**9**	H_2O_2	63	11	65	20	4
10	**10**	H_2O_2	68	10	63	23	4
11	**1**	TBHP	80	85	15	-	-
12	**2**	TBHP	81	89	11	-	-
13	**3**	TBHP	89	87	13	-	-
14	**4**	TBHP	87	84	16	-	-
15	**5**	TBHP	89	79	21	-	-
16	**6**	TBHP	82	81	19	-	-
17	**7**	TBHP	85	82	18	-	-
18	**8**	TBHP	90	84	16	-	-

19	**9**	TBHP	87	80	20	-	-
20	**10**	TBHP	83	84	16	-	-

[a] ChO – cyclohexene oxide, ChOL – 2-cyclohexene-1-ol, ChON – 2-cyclohexene-1-one, ChDL – cyclohexane-1,2-diol.

Similarly, for three different amounts (*i.e.* 0.5, 1 and 2 mol%) of catalyst and oxidant to cyclohexene molar ratio of 2:1 under above reaction conditions, 0.5 mol% gave only 22% (H_2O_2) and 31% (TBHP) oxidative conversion, while 1 mol% and 2 mol% of catalyst have shown a maximum conversion with 68% for H_2O_2 and 89% for TBHP. Thus, 1 mol% of catalyst may be considered sufficient enough to run the reaction under above conditions. A blank reaction under the above reaction conditions gave with both oxidants *ca.* 4-5% conversion.

Table 5. Catalytic oxidation of cyclohexene in presence of 1 mol% vanadium(V) Schiff base complexes in acetonitrile.

Entry	Catalyst	Oxidant	Conv. (%)	Product selectivity (%)			
				ChO	ChOL	ChON	ChDL
1	**11**	H_2O_2	42	30	31	3	36
2	**12**	H_2O_2	54	27	33	11	29
3	**13**	H_2O_2	57	35	34	4	27
4	**14**	H_2O_2	53	27	28	7	38
5	**15**	H_2O_2	55	24	30	5	41
6	**16**	H_2O_2	56	33	31	12	24
7	**17**	H_2O_2	51	30	32	5	33
8	**18**	H_2O_2	58	27	26	14	33
9	**19**	H_2O_2	52	25	33	6	36
10	**20**	H_2O_2	56	28	30	8	34
11	**11**	TBHP	85	1	90	1	8
12	**12**	TBHP	96	2	87	2	9
13	**13**	TBHP	86	3	84	2	11
14	**14**	TBHP	92	1	89	1	9
15	**15**	TBHP	96	-	86	1	13
16	**16**	TBHP	90	3	89	-	8
17	**17**	TBHP	72	4	87	1	8
18	**18**	TBHP	71	2	89	1	8
19	**19**	TBHP	89	5	86	1	8
20	**20**	TBHP	92	2	88	1	9

In these conditions, conversion of cyclohexene with 30% H_2O_2 as an oxidant (Table 4, entries 1-10) is distinctly higher than for styrene (61-70%). Surprisingly, **1**-**10** catalysts are the most selective toward 2-cyclohexene-1-ol (54-66%). Furthermore, the selectivity against 2-cyclohexene-1-one (20-29%) is more noticeable than against cyclohexene oxide (9-13%) and cyclohexane-1,2-diol (3-7%). The reason for the formation of the allylic oxidation products, *i.e.* 2-cyclohexen-1-ol and 2-cyclohexen-1-one in higher selectivity may be preferential attack of the activated C–H bond over the C=C bond [35].

When catalytic reactions have been performed under optimized conditions, but with *tert*-butyl hydroperoxide (TBHP) in decane as an oxidant (Table 4, entries 11-20), **1**-**10** gave

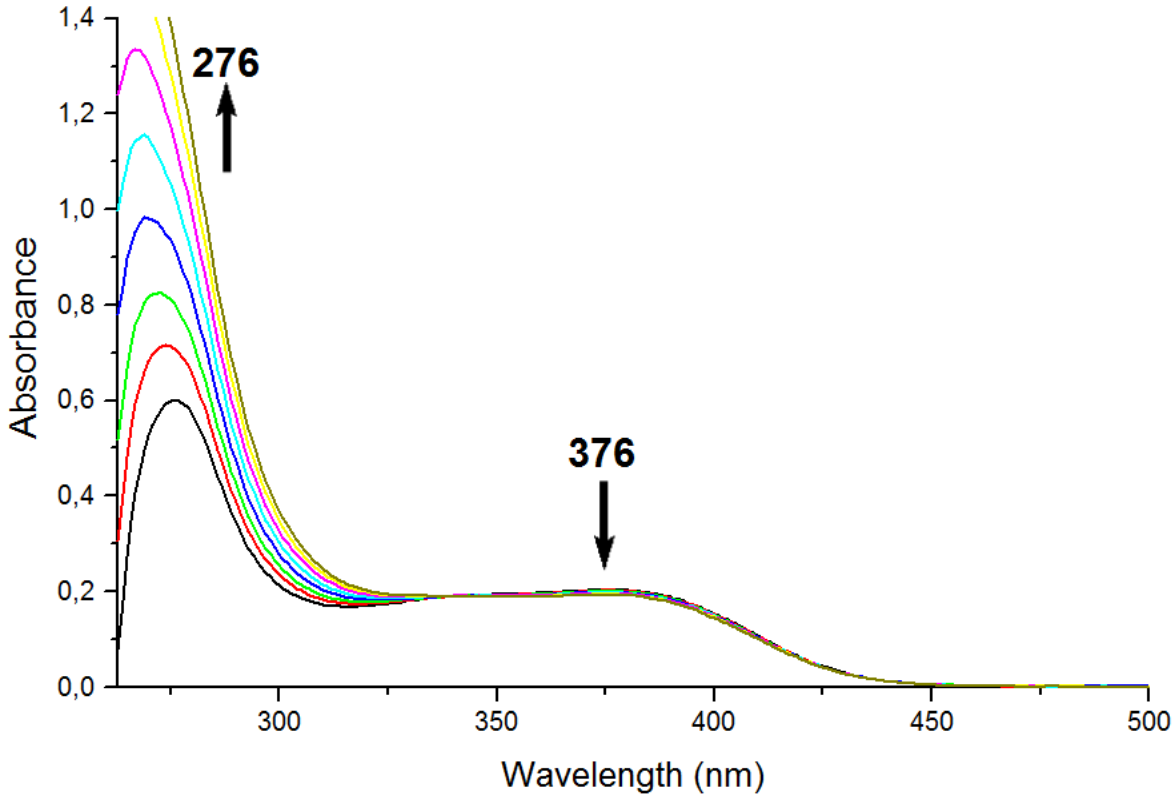
much higher conversion of cyclohexene (80-90%). In contrast to catalytic reactions with H_2O_2, molybdenum(VI) catalysts are distinctly more selective toward cyclohexene oxide (79-89%). The rest amounts of 2-cyclohexene-1-ol found in the reaction mixture are by-products. Very similar results were reported by Rayati *et al.* [24] with MoO_2{hnaphnptn} – dioxidomolybdenum(VI) complex with symmetrical tetradentate Schiff base.

Vanadium(V) complexes have been also tested in the oxidation of cyclohexene and results were compared with these for molybdenum(VI) complexes. When oxidation reactions were performed with aqueous 30% H_2O_2 as an oxidant, 42-58% conversion in acetonitrile and 6 h of contact time was found (Table 5, entries 1-10) and is distinctly lower than for **1-10.** The selectivity against cyclohexene oxide (24-35%), 2-cyclohexene-1-ol (26-34%) and cyclohexane-1,2-diol (29-41%) is almost the same, only 2-cyclohexene-1-one (3-14%) is present in the smallest amounts. When this catalytic reaction has been performed in the same reaction conditions, but with *tert*-butyl hydroperoxide (TBHP) as an oxidant, **11-20** catalysts gave very high up to 96% conversion (Table 5, entries 11-20). Surprisingly, in contrast to reactions with 30% H_2O_2 and also molybdenum(VI) catalysts with TBHP as an oxidant, only 2-cyclohexene-1-ol (84-90%) was the main product.

3.2.4. Reactivity of catalysts with H_2O_2

A variety of molybdenum(VI) complexes have been found to react with H_2O_2 to form the corresponding oxidoperoxido complexes, but the isolation of such $[MoO(O_2)]^{2+}$ Schiff base compounds was unsuccessful in our attempts. Nevertheless, to establish generation of such oxidoperoxido species and shed some light on the mechanism of these catalytic reactions UV-Vis spectroscopy was involved. Spectral changes were monitored by recording a series of spectra after the dropwise additions of DMSO solution of H_2O_2 to an example dioxidomolybdenum(VI) complex (Fig. 6).

Figure 6. Spectral changes observed during titration of **2** catalyst. The spectra recorded after successive addition of one drop portions of aqueous 30% H_2O_2 (1.70 g, 15 mmol) dissolved in 5 ml of DMSO to 2 ml of a $7.9 \cdot 10^{-5}$ M solution of **2** in DMSO.



In an example procedure, the spectra have been recorded after successive addition of one drop portions of aqueous 30% H_2O_2 (1.71 g, 15 mmol) dissolved in 5 ml of DMSO to 2 ml of *ca.* $7.9 \cdot 10^{-5}$ M solution of catalyst **2** in DMSO and the resultant spectroscopic changes are presented in Fig. 5. Such titration with a dilute solution of the complex **2** causes a decrease with only a marginal change in intensity of the 376 nm band, which belongs to a weak ligand-to-metal charge transfer (LMCT) transition. On the other hand, the strong intraligand π-π^* transition with 276 nm band increases its intensity considerably with a small shift to 267 nm and finally disappears. In our opinion these changes indicate the interaction of complex **2** with hydrogen peroxide and the plausible formation of the oxidoperoxidomolybdenum(VI) complex in DMSO, which in the catalytic reaction finally transfers oxygen to an appropriate organic substrate to give various oxidation products.

4. Conclusion

New chiral dioxidomolybdenum(VI) complexes derived from Schiff base ligands, monocondensation products of *o*-hydroxycarbonyl compounds with *1R,2S*(–)-norephedrine were synthesized and characterized by IR, CD, UV-Vis techniques and also 1D and 2D NMR spectroscopy. Moreover, the catalytic properties of the chiral catalysts in oxidation of thioanisole and olefins (styrene and cyclohexene) have been studied.

The results of sulfoxidation reactions show that the observed yield and enantiomeric excess significantly depend on the nature of the catalyst, especially in the aspect of catalysts possessing electron donating groups to attain sufficient nucleophilicity by the molybdenum atom. Finally, higher enantioselectivities can be obtain when the reactions are carried out in lower temperatures.

The catalytic potentials of the dioxidomolybdenum(VI) complexes and oxidovanadium(V) catalysts with the same chiral Schiff base ligands in oxidation of olefins have been also studied and compared, choosing the oxidation of styrene and cyclohexene as

the model reactions. The molybdenum(VI) complexes are able to catalyze the oxidative conversion of styrene to styrene oxide and benzaldehyde as main products. In comparison to vanadium(V) complexes, the selectivities against styrene oxide are much more higher using 30% H_2O_2 and slightly higher with TBHP as an oxidant. On the other hand, in the oxidation of cyclohexene much better conversions were found, especially when 30% H_2O_2 was employed as an oxidant. Moreover, the excellent conversion (up to 96%), using TBHP as an oxidant, for both molybdenum(VI) and vanadium(V) has been noted, with different compounds as the main products, *i.e.* cyclohexene oxide and 2-cyclohexene-1-ol, respectively.

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Synthesis, characterization and catalytic activity of dioxidomolybdenum(VI) complexes with tridentate Schiff bases derived from *1R,2S*(–)-norephedrine

chiral dioxidomolybdenum(VI) complexes with tridentate Schiff bases obtained by monocondensation of *1R,2S*(–)-norephedrine with salicylaldehyde and its derivatives were synthesized. The complexes were characterized by IR, CD, UV-Vis and NMR spectroscopy. Catalytic activity of these complexes were tested in the oxidation of olefins using aqueous 30% H_2O_2 or TBHP as an oxidant. Moreover, the dioxidomolybdenum(VI) complexes have also ability to catalyze the oxidation of thioanisole to methyl phenyl sulfoxide in presence of aqueous 30% H_2O_2.