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Synthesis, characterization and catalytic activity in the oxidation of sulfides and styrene of vanadium(V) complexes with tridentate Schiff base ligands

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ABSTRACT

A series of vanadium(V) complexes with chiral tridentate Schiff base ligands, obtained by a single condensation of *R*(−)-1-amino-2-propanol with salicylaldehyde and its derivatives, were prepared. The complexes were characterized by elemental analysis and by their IR, CD, UV–Vis, 1D (^{1}H, ^{51}V) and 2D (COSY, gHSQC) NMR spectra. The vanadium(V) complexes have ability to catalyze the oxidation of sulfides [PhSR (R = Me, Bz)] in good yields and enantiomeric excesses, utilizing aqueous 30% H_2O_2 or cumene hydroperoxide (CHP) as oxidant. Catalytic activity of these complexes and also derived from *R*(−)-1,2-diaminopropane, resulted in ONO- and ONN-type of tridentate ligands, respectively, were tested in the oxidation of styrene, using aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as oxidant.

1. Introduction

The interest in the chemistry of vanadium is mainly based on the discoveries of its active role in some biological systems such as vanadium-dependent haloperoxidases and nitrogenases [1–5], but also the insuline-like effect of vanadium compounds, *i.e.* stimulation of glucose uptake and inhibition of lipid breakdown [6], or its involvement in phosphate metabolizing enzymes [7].

Vanadium(V) Schiff base complexes as excellent functional models for vanadium haloperoxidases are amongst the most versatile catalysts extensively used in oxidation of (prochiral) organic sulfides to the medically and synthetically important (chiral) sulfoxides [8]. The catalytic activity of these complexes depends on the nature of the ligands as well as on the metal centers [9,10]. Enantiopure sulfoxides are valuable starting materials in asymmetric synthesis as well as important chiral ligands in enantioselective catalysis and also and as very efficient pharmaceuticals. As efficient chiral auxiliaries they lead to many important asymmetric transformations [11]. Also epoxides are very important intermediates in laboratory organic synthesis, found as intermediate products in some biosynthetic pathways. Their importance arises mainly from the ring opening of epoxides, which allows straightforward elaboration to useful generation of new carbon–carbon bonds.

Until now, vanadium(V) complexes with tridentate Schiff base ligands derived from chiral and achiral amino alcohols have been used successfully as catalysts in the enantioselective oxidation of organic sulfides [12,13], the asymmetric alkynylation of aldehydes [13], the epoxidation of cyclooctene [14], the oxidation of bromide [15], the stereoselective synthesis of functionalized tetrahydrofurans [15,16] and oxidative kinetic resolution of α-hydroxy esters [17]. Moreover, dioxidovanadium(V) Schiff base complexes have been found to be efficient catalysts in the oxidation of styrene utilizing H_2O_2 and TBHP as oxidants [18].

In continuation of my studies on synthesis, structure, spectroscopic and catalytic properties of vanadium(V) complexes incorporating chiral tridentate Schiff base ligands [19–21], new oxidovanadium(V) complexes with ONO donor ligands, products of monocondensation of *R*(−)-1-amino-2-propanol with aromatic *o*-hydroxyaldehydes presented in Fig. 1, have been described. Their spectroscopic properties by 1D and 2D NMR, UV–Vis, CD and IR have been examined. The catalytic potential of these complexes in the asymmetric oxidation, *i.e.* enantioselective sulfoxidation of methyl phenyl sulfide (PhSMe) and benzyl phenyl sulfide (PhSBz) utilizing aqueous 30% H_2O_2 or cumene hydroperoxide (CHP) as oxidant has been studied. Moreover, they were also used as catalysts in the oxidation of styrene, using aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as oxidant, to styrene oxide, benzaldehyde, benzoic acid, phenylacetaldehyde and 1-phenylethane-1,2-diol. For comparison, the catalytic activity in the styrene oxidation of very similar dioxidovanadium(V) complexes with ONN-type tridentate Schiff bases derived from *R*(−)-1,2-diaminopropane, synthesized and characterized earlier [21], under the same reaction conditions has been also tested.

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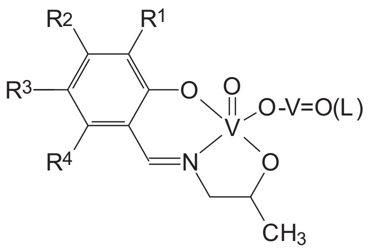


	R^1	R^2	R^3	R^4
1	H	H	H	H
2	OCH_3	H	H	H
3	H	H	OCH_3	H
4	H	OCH_3	H	OCH_3
5	H	H	CH_3	H
6	H	H	Br	H
7	H	H	NO_2	H
8	H	OH	H	H
9	$C(CH_3)_3$	H	H	H
10	H	H	$-(CH)_4-$	

Fig. 1. Structural formulae of vanadium(V) complexes.

2. Experimental

2.1. Measurements

All reagents and solvents were obtained from local sources and Sigma–Aldrich and used without further purification. 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 CD_3OD solutions with a Varian Mercury-400BB (400 MHz) spectrometer using TMS (^1H) and $VOCl_3$ (^{51}V) as reference compounds. A Perkin-Elmer Clarus 500 gas chromatograph with a DB-5 capillary column (30 m × 0.25 mm × 0.25 mm) and FID detector was used to analyze the reaction products. 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 solution (7:3, v/v), sulfide (1.00 mmol) was added at room temperature or −20 °C, together with 1,3,5-trimethoxybenzene as internal standard. Aqueous 30% H_2O_2 or cumene hydroperoxide (CHP) as oxidant was added (1.10 mmol) by small portions and the resulting mixture was stirred. After the appropriate reaction time, the solution was quenched with 2 ml of sodium sulfite solution (0.1 M) and extracted with CH_2Cl_2 (3 × 5 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) [22].

2.2.2. Oxidation of styrene

In typical procedure, styrene (1.00 mmol), an oxidant (3.00 mmol), *i.e.* aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) in 5.5 M decane, and catalyst (0.010 mmol) were taken in 10 ml of CH_3CN and the reaction was carried out for 6 h at 80 °C. The reaction was monitored by GC and the yields were recorded as GC yield based on the starting styrene. Absolute calibration curve method was used to quantify reactions products. The identity of oxidation products was confirmed by GC–MS. The influence of amounts of catalyst and oxidant was also studied to check their effect on the conversion and selectivity of the reaction products.

2.3. Complexes

The complexes were obtained by methods analogous to the literature procedure [16]. A solution of 5 mmol of *R*(−)-1-amino-2-propanol in 10 ml absolute ethanol was added with stirring to 5 mmol of an aromatic *o*-hydroxyaldehyde (salicylaldehyde, 3-methoxysalicylaldehyde, 5-methoxysalicylaldehyde, 4,6-dimethoxysalicylaldehyde, 5-methylsalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, 2,4-dihydroxybenzaldehyde, 3-*tert*-butylsalicylaldehyde, 2-hydroxy-1-naphthaldehyde) in 20 ml absolute EtOH and heated under reflux for 1 h. Then a vanadium(V) oxytriethoxide (5 mmol) in 10 ml of absolute EtOH was added and stirred at room temperature for 2 h. After cooling in a fridge a solid was separated and filtered off, washed several times and recrystallized from absolute EtOH.

2.3.1. *μ-Oxido-bis({R(−)-2-[(2-oxidopropyl)iminomethyl]phenolato-κ³N,O,O'}oxidovanadium(V))* (***1***)

Yield 78%. *Anal.* Calc. for $C_{20}H_{22}N_2O_7V_2$: C, 47.6; H, 4.4; N, 5.6. Found: C, 47.5; H, 4.5; N, 5.7. IR (KBr, cm^{-1}): 1639 ($\nu_{C=N}$); 973 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε ($M^{-1}\,cm^{-1}$)]: 278 (9850), 329 (4400). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ ($M^{-1}\,cm^{-1}$)]: 252 (−4.14), 285 (3.49), 356 (−8.53). ^1H NMR (CD_3OD, ppm) major (60%): 8.66 (1H, s) (azomethine); 7.52 (2H, m), 6.94 (2H, m) (aromatic); 5.22 (1H, m) (methine); 4.41 (1H, dd, $^3J = 8$ Hz, $^4J = 3$ Hz), 3.65 (1H, dd, $^3J = 8$ Hz, $^4J = 6$ Hz) (methylene); 1.35 (3H, d, $^3J = 8$ Hz) (methyl); minor (40%): 8.64 (1H, s) (azomethine); 7.53 (2H, ov), 6.95 (2H, ov) (aromatic); 4.96 (1H, m) (methine); 4.33 (1H, dd, $^3J = 8$ Hz, $^4J = 6$ Hz), 4.09 (1H, dd, $^3J = 8$ Hz, $^4J = 3$ Hz) (methylene); 1.47 (3H, d, $^3J = 8$ Hz) (methyl). ^{51}V NMR (CD_3OD, ppm) major (60%): −540.5, minor (40%): −537.6.

2.3.2. *μ-Oxido-bis({R(−)-2-[(2-oxidopropyl)iminomethyl]-6-methoxyphenolato-κ³N,O,O'}oxidovanadium(V))* (***2***)

Yield 81%. *Anal.* Calc. for $C_{22}H_{26}N_2O_9V_2$: C, 46.8; H, 4.6; N, 5.0. Found: C, 46.7; H, 4.5; N, 5.1. IR (KBr, cm^{-1}): 1630 ($\nu_{C=N}$); 971 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε ($M^{-1}\,cm^{-1}$)]: 285 (9710), 353 (4270). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ ($M^{-1}\,cm^{-1}$)]: 254 (−3.42), 281 (2.87) 366 (−6.15). ^1H NMR (CD_3OD, ppm) major (60%): 8.68 (1H, s) (azomethine); 7.18 (1H, t, $^3J = 8$ Hz) 7.14 (1H, d, $^3J = 8$ Hz), 6.88 (1H, t, $^3J = 8$ Hz) (aromatic); 5.20 (1H, m) (methine); 4.44 (1H, dd, $^3J = 8$ Hz, $^4J = 3$ Hz), 3.68 (1H, dd, $^3J = 8$ Hz, $^4J = 6$ Hz) (methylene); 1.37 (3H, d, $^3J = 8$ Hz) (methyl); 3.92 (3H, s) (methoxy); minor (40%): 8.66 (1H, s) (azomethine); 7.19 (1H, ov), 7.15 (1H, ov), 6.89 (1H, ov) (aromatic); 4.96 (1H, m) (methine); 4.32 (1H, dd, $^3J = 8$ Hz, $^4J = 6$ Hz), 4.14 (1H, dd, $^3J = 8$ Hz, $^4J = 3$ Hz) (methylene); 1.44 (3H, d, $^3J = 8$ Hz) (methyl); 3.87 (3H, s) (methoxy). ^{51}V NMR (CD_3OD, ppm) major (60%): −537.1, minor (40%): −533.6.

*2.3.3. μ-Oxido-bis({R(−)-2-[(2-oxidopropyl)iminomethyl]-4-methoxyphenolato-κ^3N,O,O'}oxidovanadium(V)) (**3**)*

Yield 75%. *Anal.* Calc. for $C_{22}H_{26}N_2O_9V_2$: C, 46.8; H, 4.6; N, 5.0. Found: C, 46.9; H, 4.7; N, 5.1. IR (KBr, cm^{-1}): 1632 ($\nu_{C=N}$); 972 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 284 (9680), 351 (4230). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 254 (−3.37), 284 (2.65), 355 (−5.94). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.68 (1H, s) (azomethine); 7.19 (2H, m), 6.93 (1H, t, ^{3}J = 8 Hz) (aromatic); 5.21 (1H, m) (methine); 4.45 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz), 3.69 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz) (methylene); 1.36 (3H, d, ^{3}J = 8 Hz) (methyl); 3.90 (3H, s) (methoxy); minor (40%): 8.66 (1H, s) (azomethine); 7.20 (2H, ov), 6.94 (1H, ov) (aromatic); 5.00 (1H, m) (methine); 4.32 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz), 4.13 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz) (methylene); 1.45 (3H, d, ^{3}J = 8 Hz) (methyl); 3.85 (3H, s) (methoxy). ^{51}V NMR (CD_3OD, ppm) major (60%): −537.7, minor (40%): −534.2.

*2.3.4. μ-Oxido-bis({R(−)-2-[(2-oxidopropyl)iminomethyl]-3,5-dimethoxyphenolato-κ^3N,O,O'}oxidovanadium(V)) (**4**)*

Yield 77%. *Anal.* Calc. for $C_{24}H_{30}N_2O_{11}V_2$: C, 46.2; H, 4.8; N, 4.5. Found: C, 46.0; H, 4.8; N, 4.4. IR (KBr, cm^{-1}): 1602 ($\nu_{C=N}$); 973 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 317 (17,660). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 252 (−2.86), 285 (2.52), 350 (−4.22). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.87 (1H, s) (azomethine); 6.23 (1H, d, ^{4}J = 3 Hz), 6.17 (1H, d, ^{4}J = 3 Hz) (aromatic); 5.17 (1H, m) (methine); 4.42 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz), 3.66 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz) (methylene); 1.34 (3H, d, ^{3}J = 8 Hz) (methyl); 3.89 (3H, s), 3.85 (3H, s) (methoxy); minor (40%): 8.85 (1H, s) (azomethine); 6.19 (1H, ov), 6.15 (1H, ov) (aromatic); 4.96 (1H, m) (methine); 4.30 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz), 4.06 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz) (methylene); 1.42 (3H, d, ^{3}J = 8 Hz) (methyl); 3.90 (3H, ov), 3.86 (3H, ov) (methoxy). ^{51}V NMR (CD_3OD, ppm) major (60%): −538.3, minor (40%): −536.2.

*2.3.5. μ-Oxido-bis({R(−)-2-[(2-oxidopropyl)iminomethyl]-4-methylphenolato-κ^3N,O,O'}oxidovanadium(V)) (**5**)*

Yield 79%. *Anal.* Calc. for $C_{22}H_{26}N_2O_7V_2$: C, 49.6; H, 4.9; N, 5.3. Found: C, 49.5; H, 4.8; N, 5.5. IR (KBr, cm^{-1}): 1636 ($\nu_{C=N}$); 970 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 278 (9830), 327 (4370). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 254 (−4.12), 299 (3.31), 360 (−10.28). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.62 (1H, s) (azomethine); 7.31 (2H, m) 6.84 (1H, d, ^{3}J = 8 Hz) (aromatic); 5.20 (1H, m) (methine); 4.47 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz), 3.66 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz) (methylene); 2.32 (1H, s), 1.33 (3H, d, ^{3}J = 8 Hz) (methyl); minor (40%): 8.64 (1H, s) (azomethine); 7.33 (2H, ov), 6.86 (1H, ov) (aromatic); 4.96 (1H, m) (methine); 4.36 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz), 4.08 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz) (methylene); 2.33 (1H, ov), 1.45 (3H, d, ^{3}J = 8 Hz) (methyl). ^{51}V NMR (CD_3OD, ppm) major (60%): −537.9, minor (40%): −533.8.

*2.3.6. μ-Oxido-bis({R(−)-2-[(2-oxidopropyl)iminomethyl]-4-bromophenolato-κ^3N,O,O'}oxidovanadium(V)) (**6**)*

Yield 81%. *Anal.* Calc. for $Br_2C_{20}H_{20}N_2O_7V_2$: C, 36.3; H, 3.0; N, 4.2. Found: C, 36.4; H, 3.2; N, 4.2. IR (KBr, cm^{-1}): 1634 ($\nu_{C=N}$); 974 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 282 (10,040), 330 (4940). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 253 (−3.91), 285 (2.28), 361 (−6.32). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.73 (1H, s) (azomethine); 7.66 (1H, d, ^{4}J = 3 Hz), 7.56 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz), 6.87 (1H, d, ^{3}J = 8 Hz) (aromatic); 5.24 (1H, m) (methine); 4.39 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz), 3.62 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz) (methylene); 1.39 (3H, d, ^{3}J = 8 Hz) (methyl); minor (40%): 8.74 (1H, ov) (azomethine); 7.64 (1H, ov), 7.54 (1H, ov), 6.92 (1H, d, ^{3}J = 8 Hz) (aromatic); 4.91 (1H, m) (methine); 4.30 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz), 4.06 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz) (methylene); 1.51 (3H, d, ^{3}J = 8 Hz) (methyl). ^{51}V NMR (CD_3OD, ppm) major (60%): −539.9, minor (40%): −538.1.

*2.3.7. μ-Oxido-bis({R(−)-2-[(2-oxidopropyl)iminomethyl]-4-nitrophenolato-κ^3N,O,O'}oxidovanadium(V)) (**7**)*

Yield 74%. *Anal.* Calc. for $C_{20}H_{20}N_4O_{11}V_2$: C, 40.4; H, 3.4; N, 9.4. Found: C, 40.3; H, 3.6; N, 9.3. IR (KBr, cm^{-1}): 1643 ($\nu_{C=N}$); 975 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 347 (14,840). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 255 (−4.23), 314 (4.33), 359 (−7.02). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.72 (1H, s) (azomethine); 8.49 (1H, d, ^{4}J = 3 Hz), 8.29 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz), 6.99 (1H, d, ^{3}J = 8 Hz) (aromatic); 5.41 (1H, m) (methine); 4.42 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz), 3.75 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz) (methylene); 1.37 (3H, d, ^{3}J = 8 Hz) (methyl); minor (40%): 8.73 (1H, ov) (azomethine); 8.48 (1H, ov), 8.27 (1H, ov), 7.05 (1H, d, ^{3}J = 8 Hz) (aromatic); 4.95 (1H, m) (methine); 4.25 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz), 4.02 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz) (methylene); 1.45 (3H, d, ^{3}J = 8 Hz) (methyl). ^{51}V NMR (CD_3OD, ppm) major (60%): −536.7, minor (40%): −539.7.

*2.3.8. μ-Oxido-bis({R(−)-2-[(2-oxidopropyl)iminomethyl]-5-hydroxyphenolato-κ^3N,O,O'}oxidovanadium(V)) (**8**)*

Yield 80%. *Anal.* Calc. for $C_{20}H_{22}N_2O_9V_2$: C, 44.8; H, 4.1; N, 5.2. Found: C, 44.7; H, 4.2; N, 5.1. IR (KBr, cm^{-1}): 1599 ($\nu_{C=N}$); 961 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 288 (9910), 350 (4620). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 253 (−3.44), 282 (3.39), 351 (−5.40). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.58 (1H, s) (azomethine); 7.41 (1H, t, ^{3}J = 8 Hz), 6.47 (1H, t, ^{3}J = 8 Hz), 6.35 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz) (aromatic); 5.30 (1H, m) (methine); 4.40 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz), 3.66 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz) (methylene); 1.39 (3H, d, ^{3}J = 8 Hz) (methyl); minor (40%): 8.59 (1H, ov) (azomethine); 7.42 (1H, ov), 6.46 (1H, ov), 6.34 (1H, ov) (aromatic); 5.10 (1H, m) (methine); 4.28 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz), 4.05 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz) (methylene); 1.46 (3H, d, ^{3}J = 8 Hz) (methyl). ^{51}V NMR (CD_3OD, ppm) major (60%): −536.1, minor (40%): −538.9.

*2.3.9. μ-Oxido-bis({R(−)-2-[(2-oxidopropyl)iminomethyl]-6-tert-butylphenolato-κ^3N,O,O'}oxidovanadium(V)) (**9**)*

Yield 77%. *Anal.* Calc. for $C_{28}H_{38}N_2O_7V_2$: C, 54.6; H, 6.2; N, 4.5. Found: C, 54.7; H, 6.3; N, 4.4. IR (KBr, cm^{-1}): 1635 ($\nu_{C=N}$); 975 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 277 (9680), 328 (4120). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 256 (−2.65), 295 (2.33), 359 (−6.41). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.76 (1H, s) (azomethine); 7.47 (1H, d, ^{3}J = 8 Hz), 7.32 (1H, d, ^{3}J = 8 Hz), 6.80 (1H, t, ^{3}J = 8 Hz) (aromatic); 5.27 (1H, m) (methine); 4.38 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz), 3.64 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz) (methylene); 1.38 (3H, d, ^{3}J = 8 Hz) (methyl); 1.49 (9H, s) (*tert*-butyl); minor (40%): 8.78 (1H, s) (azomethine); 7.48 (1H, ov), 7.33 (1H, ov), 6.84 (1H, t, ^{3}J = 8 Hz) (aromatic); 5.01 (1H, m) (methine); 4.26 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz), 4.03 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz) (methylene); 1.46 (3H, d, ^{3}J = 8 Hz) (methyl); 1.48 (9H, ov) (*tert*-butyl). ^{51}V NMR (CD_3OD, ppm) major (60%): −550.4, minor (40%): −553.6.

*2.3.10. μ-Oxido-bis({R(−)-2-[(2-oxidopropyl)iminomethyl]naphtholato-κ^3N,O,O'}oxidovanadium(V) (**10**)*

Yield 74%. *Anal.* Calc. for $C_{28}H_{26}N_2O_7V_2$: C, 55.6; H, 4.3; N, 4.6. Found: C, 55.5; H, 4.4; N, 4.7. IR (KBr, cm^{-1}): 1622 ($\nu_{C=N}$); 978 ($\nu_{V=O}$).

UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 309 (8980), 395 (3770). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 253 (−2.69), 291 (2.19), 363 (−4.97). ^{1}H NMR (CD_3OD, ppm) major (60%): 9.55 (1H, s) (azomethine); 8.28 (1H, d, ^{3}J = 8 Hz), 8.01 (1H, d, ^{3}J = 8 Hz), 7.84 (1H, d, ^{3}J = 8 Hz), 7.60 (1H, t, ^{3}J = 8 Hz), 7.40 (1H, t, ^{3}J = 8 Hz), 7.17 (1H, d, ^{3}J = 8 Hz) (aromatic); 5.27 (1H, m) (methine); 4.62 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz), 3.81 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz) (methylene); 1.39 (3H, d, ^{3}J = 8 Hz) (methyl); minor (40%): 9.56 (1H, s) (azomethine); 8.58 (1H, d, ^{3}J = 8 Hz), 8.16 (1H, d, ^{3}J = 8 Hz), 8.07 (1H, d, ^{3}J = 8 Hz), 7.74 (1H, t, ^{3}J = 8 Hz), 7.29 (1H, t, ^{3}J = 8 Hz), 7.04 (1H, d, ^{3}J = 8 Hz) (aromatic); 5.04 (1H, m) (methine); 4.48 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 6 Hz), 4.29 (1H, dd, ^{3}J = 8 Hz, ^{4}J = 3 Hz) (methylene); 1.46 (3H, d, ^{3}J = 8 Hz) (methyl). ^{51}V NMR (CD_3OD, ppm) major (60%): −541.9, minor (40%): −538.9.

3. Results and discussion

3.1. Spectroscopic properties

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

The IR spectra of solid complexes display strong C═N stretch (around 1600–1640 cm^{-1}) which indicates the C═N group of the coordinated Schiff base ligands [23,24]. These vanadium(V) species also show absorption bands around 960–980 cm^{-1}, attributable to single V═O stretching vibrations, which are close to values reported for related oxidovanadium(V) Schiff base complexes [14,16]. The appearance of weak/medium band near 2800 cm^{-1} separate from other C—H stretching vibrations in **2**, **3**, **4** complexes indicated the presence of the methoxy substituents [25].

The electronic and circular dichroism spectra of all complexes were recorded in methanol. Strong intense bands, ε_{max} = 8980–10,040 dm^3 mol^{-1} cm^{-1}, with λ_{max} in region 278–309 nm are considered to arise from intraligand π–π^* transitions. The low energy bands, recorded for **1–3**, **5**, **6**, **8–10** complexes, between 327 and 395 nm (ε_{max} = 3770–4940 dm^3 mol^{-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 at the vanadium(V) center [26,27]. The spectra of **4** and **7** complexes examined in the same spectral region display only one very strong bands at 317 (ε_{max} = 17,660) and 347 (ε_{max} = 14,840) nm, respectively, similar to the same strong bands at around 320 and 350 nm for complexes derived from 4,6-dimethoxysalicylaldehyde and 5-nitrosalicylaldehyde [15,19,20]. The circular dichroism spectra revealed an additional band in the 281–314 nm range with opposite sign of the Cotton effect to the bands at around 250 and 360 nm.

^{1}H NMR signals were assigned on the basis of intensity, spin–spin coupling pattern, chemical shifts, COSY and gHSQC techniques. Single condensation of salicylaldehyde and its derivatives with 1-amino-2-propanol is confirmed by the presence of azomethine proton signals in the spectra of all complexes. Signals of the methyl and methine protons in all compounds have been readily recognized. For this purpose 2D (COSY, gHSQC) NMR spectroscopy was performed for all complexes and allow to unambiguously establish the attachment of carbon atoms in the 1-amino-2-propanolate fragment. For example, in case of COSY spectrum of **5**, cross-peaks between the methine proton signal (major species signal at 5.03 ppm) and two methylene protons doublet of doublets (at 4.47 and 3.66 ppm), and also methyl proton doublet at 1.33 ppm are observed. Moreover, NOESY spectra exhibit cross-peaks between the signal of the azomethine proton (major species signal at 8.62 ppm) and two of the methylene protons (4.47 and 3.66 ppm) and, as expected, there is no corresponding cross-peaks between the signals of the azomethine proton and the methine proton (5.20 ppm) or the methyl proton (1.33 ppm).

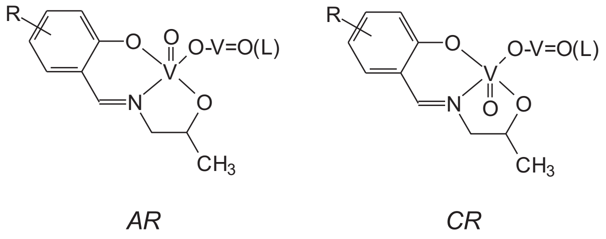


Fig. 2. Visualization of *AR* and *CR* diastereomers caused by dissymmetric vanadium(V) ions.

In the ^{1}H NMR spectra in CD_3OD, two sets of signals are observed to suggest the presence of two species in solution. Chemical shifts for the two species are listed separately and designated as major and minor. In all cases, the major:minor ratios are about 60:40, in contrast to similar vanadium(V) Schiff base complexes derived from different amino alcohols, where contribution of major species varies from 53 to 95% [13]. The ^{51}V NMR spectra exhibit two signals with the same major:minor ratios as the signals in the ^{1}H NMR spectra. According to Rehder et al. [28], possible reasons for presence of two species in solution could be diastereomers, equilibria between monomeric and dimeric (or oligomeric) complexes or flexibility with respect to the coordination geometry and the arrangement of the ligands. When dimers or oligomers are formed temperature dependence of chemical shift and the increasing intensity of signals with an increase of the concentration of complexes should be observed in ^{51}V NMR spectra. These rather high-field resonances are present in chloroform solution [29] and disappear when methanol is used as solvent, due to an additional coordination of methanol leading to six-coordinated vanadium species. We assume that in our case the existence of two diastereomers (*AR* and *CR*), caused by chiral *R* methine carbon atom in the 1-amino-2-propanolate moiety and two possible (clockwise – *C* and anti-clockwise – *A*) absolute configurations at vanadium atom (Fig. 2), is the most likely explanation for presence of two ^{51}V NMR signals [30,31].

3.2. Catalytic activity studies

3.2.1. Sulfoxidation

In this study, the oxidovanadium(V) complexes **1–10** for their ability to catalyze the oxidation of prochiral sulfides using methyl phenyl sulfide (thioanisol) and phenyl benzyl sulfide as model substrates have been tested (Fig. 3). Aqueous 30% H_2O_2 or cumene hydroperoxide (CHP) were used as oxidant in a slight excess of 1.10 equivalents based on the sulfide substrate. Reactions were run with 1 mol% of catalyst based on the model substrate. The results of catalytic studies are listed in Table 1.

The best results have been obtained for complexes **2**, **3**, **5**, **6** and **8** as catalysts in the oxidation of methyl phenyl sulfide with 30% H_2O_2 as oxidant (Table 1, entries 2, 3, 5, 6 and 8). An overall yields for all catalysts were in the range of 83–91% within 30 min reaction time and enantiomeric excess (ee's) of 26–39% of the R-configured sulfoxide was obtained. For the same time of reaction, with **2**, **3**, **5**, **6**, **8** catalysts and methyl phenyl sulfide, but employing CHP as oxidant, similar yield (81–98%) but lower ee's values (26–30%) of the R-configured sulfoxide were obtained (Table 1, entries 16–20).

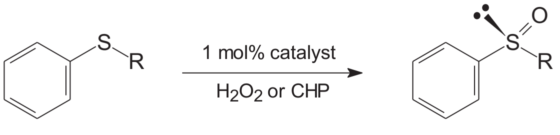


Fig. 3. Sulfoxidation of thioethers catalyzed by vanadium(V) complexes.

Table 1
Catalytic oxidation of PhSMe and PhSBz by 30% H_2O_2 or cumene hydroperoxide (CHP) as oxidant in presence of 1 mol% vanadium(V) Schiff base complexes as catalysts.

Entry	Catalyst	Substrate	Oxidant	Yield (%)	*T* (°C)	*t* (min)	*ee* (%)[a]
1	**1**	PhSMe	H_2O_2	84	rt	30	30
2	**2**	PhSMe	H_2O_2	86	rt	30	39
3	**3**	PhSMe	H_2O_2	85	rt	30	38
4	**4**	PhSMe	H_2O_2	84	rt	30	29
5	**5**	PhSMe	H_2O_2	87	rt	30	37
6	**6**	PhSMe	H_2O_2	91	rt	30	36
7	**7**	PhSMe	H_2O_2	84	rt	30	31
8	**8**	PhSMe	H_2O_2	83	rt	30	39
9	**9**	PhSMe	H_2O_2	87	rt	30	26
10	**10**	PhSMe	H_2O_2	86	rt	30	27
11	**2**	PhSBz	H_2O_2	74	rt	30	14
12	**3**	PhSBz	H_2O_2	71	rt	30	12
13	**5**	PhSBz	H_2O_2	73	rt	30	18
14	**6**	PhSBz	H_2O_2	75	rt	30	14
15	**8**	PhSBz	H_2O_2	75	rt	30	15
16	**2**	PhSMe	CHP	81	rt	30	29
17	**3**	PhSMe	CHP	89	rt	30	28
18	**5**	PhSMe	CHP	84	rt	30	26
19	**6**	PhSMe	CHP	83	rt	30	28
20	**8**	PhSMe	CHP	87	rt	30	30
21	**2**	PhSMe	H_2O_2	86	−20	180	46
22	**3**	PhSMe	H_2O_2	84	−20	180	44
23	**5**	PhSMe	H_2O_2	86	−20	180	43
24	**6**	PhSMe	H_2O_2	89	−20	180	46
25	**8**	PhSMe	H_2O_2	87	−20	180	45

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

When benzyl phenyl sulfide was used as substrate, possessing more bulky substituent, with hydrogen peroxide as oxidant, the overall yield of sulfoxide was distinctly lower (71–75%) and enantioselectivity decreases to value of 12–18% (Table 1, entry 11–15). With the reaction carried out at −20 °C with 30% H_2O_2 as oxidant, for **2**, **3**, **5**, **6** and **8** as catalysts, enantioselectivities improve significantly to 43–46% ee and a conversion of over 84% of the substrate is observed after 3 h (Table 1, entries 21–25). Mimoun et al. [32] pointed out the importance of sufficiently nucleophilic center for the oxidative catalysis of organic substances by peroxidovanadium(V) compounds. Better enantioselectivities for **2**, **3**, **5**, **6** and **8** as compared to other catalysts may be result of a higher electron density on the phenolato oxygen, *e.g.* due to the electronic effects of orto-, meta- and para-substituted groups, contributing to an attainment of sufficient nucleophilicity by the vanadium center.

In general, the best results have been obtained in the oxidation reactions of methyl phenyl sulfide with 30% H_2O_2 as oxidant. Significant decrease in reactivity is observed, *i.e.* enantioselectivity as well as the overall yield of the oxidation of PhSMe, when the bulkier oxidant cumene hydroperoxide as oxidant has been employed. Moreover, increasing the steric demand of the substrate on going from methyl phenyl sulfide to benzyl phenyl sulfide leads to a decrease in both the overall yield and enantioselectivity of corresponding sulfoxide. In contrast to chiral oxidovanadium(V) Schiff base complexes derived from optically active diamines used as catalysts in the sulfoxidation reactions significantly shorter reaction times and much higher values of enantiomeric excesses of corresponding sulfoxides employing **1**–**10** as catalysts were observed [19–21]. A mechanism of enantioselective sulfoxidation catalyzed by vanadium(V) Schiff base complexes, **1**–**10**, is also proposed (Fig. 4).

3.2.2. Oxidation of styrene

The catalytic potential of the **1–10** complexes have been found for the oxidation of styrene in presence of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as oxidant to give styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde (Fig. 5). The formation of all these products is presented in Table 2.

In order to achieve suitable reaction conditions for a maximum oxidative conversion of styrene, complex **7** was taken as a representative catalyst and different parameters, *i.e.* amount of catalyst (0.5, 1 and 2 mol%) and oxidant (1:1, 2:1 and 3:1 molar ratios to styrene) were tested.

For three different molar ratios of styrene to aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) in decane (*i.e.* 1:1, 1:2 and 1:3), styrene (1.00 mmol) and catalyst (0.010 mmol) were taken in CH_3CN (10 ml), and the reaction was carried out for 6 h of contact time at 80 °C. At a 30% H_2O_2 to styrene molar ratio of 1:1, a maximum of 5.1% conversion was achieved. Increasing the ratio to 2:1 improved the conversion to 18.4%, while 3:1 ratio has shown a maximum of 27.5% conversion. Further increment of H_2O_2 shows no improvement in conversion, therefore a 3:1 ratio being considered adequate. In case of using TBHP as oxidant, increasing the TBHP/styrene ratio from 1:1 to 2:1 and 3:1 improved the conversion from 41.8 to 73.6 and 99.2%, respectively. As in the previous case the oxidation improved only marginally upon further addition of oxidant.

Similarly for three different amounts (*i.e.* 0.5, 1 and 2 mol%) of catalyst and oxidant to styrene molar ratio of 3:1 under above reaction conditions, 0.5 mol% gave only 10.4%, in case of using H_2O_2, and 53.7% (TBHP) oxidative conversion, while 1 and 2 mol% have shown nearly identical results with 27.5 and 99.2% conversion, for H_2O_2 and TBHP, respectively, for 6 h of contact time. 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.* 2–3% conversion.

Using *tert*-butyl hydroperoxide (TBHP) as oxidant, under the optimized reaction conditions (*i.e.* 1.00 mmol of styrene, 3.00 mmol of oxidant, 1 mol% of catalyst), all the complexes gave excellent over 90% conversion. Table 2 summarizes the percentage conversion of styrene and the selectivities for the various reaction products. Selectivity, in case of all vanadium(V) complexes, is rather similar and they are generally distinctly more selective toward benzaldehyde (54.4–63.7%) than styrene oxide (17.0–25.4%). The conversion of the other oxidation products is low (>12%) and the selectivity varies in the order: benzoic acid > 1-phenylethane-1,2-diol > phenylacetaldehyde. When this catalytic reaction have been performed in the same reaction conditions, but with 30% H_2O_2

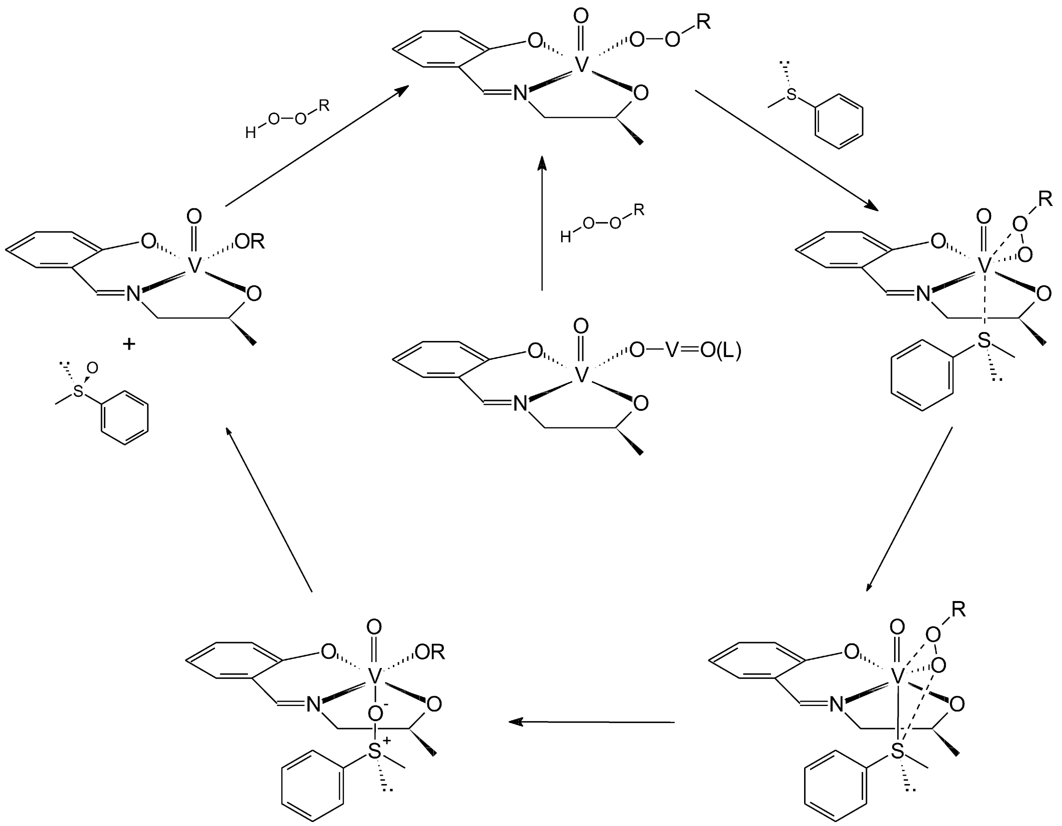


Fig. 4. Proposed mechanism for enantioselective sulfoxidation.

as oxidant, very low conversion in 6 h of contact time was found (*ca.* 25%). Although the conversion of styrene is distinctly low, the selectivity for benzaldehyde (main product) is much better (80.3–86.8%) than in the case of TBHP. The selectivity for the other oxidation product follows the order 1-phenylethane-1,2-diol (*ca.* 10%) ≫ styrene oxide > phenylacetaldehyde > benzoic acid.

For comparison, very similar dioxidovanadium(V) complexes but with ONN-type tridentate Schiff bases derived from *R*(−)-1,2-diaminopropane, **11**–**20**, have been tested as catalysts, employing the same oxidants and under the same optimized reaction conditions (Fig. 6). Synthesis, structure, spectroscopic characterization and catalytic properties in asymmetric sulfoxidation of these compounds have been reported earlier [21]. Using TBHP as oxidant, conversion goes down considerably to 70.5–86.3%, especially in the case of catalysts derived from *o*-hydroxyketones, **18**–**20**, but is still much better than in case of

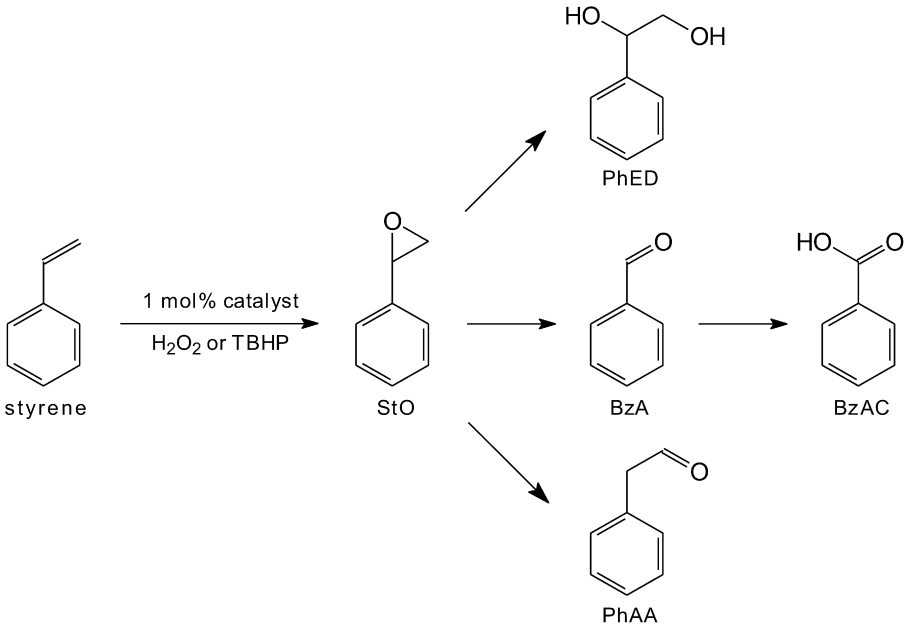
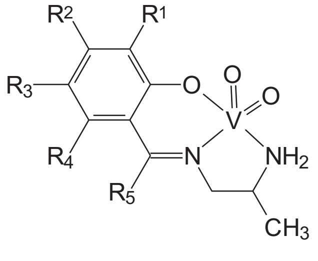


Fig. 5. Various oxidation products of styrene catalyzed by vanadium(V) complexes.

Table 2
Catalytic oxidation of styrene by 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as oxidant in presence of 1 mol% vanadium(V) Schiff base complexes as catalysts.

Entry	Catalyst	Oxidant	Conv. (%)	Product selectivity (%)				
				StO[a]	BzA[b]	BzAC[c]	PhAA[d]	PhED[e]
1	**1**	H_2O_2	22.5	2.9	83.8	1.1	1.9	10.3
2	**2**	H_2O_2	24.2	2.4	84.6	1.9	2.2	8.9
3	**3**	H_2O_2	25.7	2.6	84.7	1.3	2.0	9.4
4	**4**	H_2O_2	24.3	2.7	83.3	1.2	2.9	9.9
5	**5**	H_2O_2	26.3	2.1	85.8	1.5	2.5	8.1
6	**6**	H_2O_2	25.8	2.9	84.1	2.0	2.8	8.2
7	**7**	H_2O_2	27.5	1.8	86.8	1.9	2.2	7.3
8	**8**	H_2O_2	23.6	2.5	83.5	1.7	2.9	9.4
9	**9**	H_2O_2	24.1	2.8	81.5	1.8	2.5	11.4
10	**10**	H_2O_2	21.3	3.5	80.3	2.5	4.0	9.7
11	**1**	TBHP	92.4	23.4	54.4	11.4	2.6	8.2
12	**2**	TBHP	94.7	21.7	55.7	11.8	2.9	7.9
13	**3**	TBHP	96.1	22.3	57.1	11.7	2.1	6.8
14	**4**	TBHP	95.3	20.1	58.4	11.2	2.0	8.3
15	**5**	TBHP	96.7	17.0	61.7	10.1	1.7	9.5
16	**6**	TBHP	93.2	18.6	60.9	10.4	2.0	8.1
17	**7**	TBHP	99.2	25.4	55.4	10.7	2.6	5.9
18	**8**	TBHP	94.6	18.8	59.5	11.5	2.8	7.4
19	**9**	TBHP	90.3	23.1	57.2	10.2	2.3	7.2
20	**10**	TBHP	92.7	19.3	55.8	11.6	2.9	10.4
21	**11**	H_2O_2	17.7	2.9	82.4	–	0.9	13.8
22	**12**	H_2O_2	16.3	2.7	84.6	–	0.6	12.1
23	**13**	H_2O_2	17.5	2.1	85.5	–	0.7	11.7
24	**14**	H_2O_2	18.8	2.4	83.8	–	0.7	13.1
25	**15**	H_2O_2	16.2	2.2	86.1	–	0.8	10.9
26	**16**	H_2O_2	18.5	1.5	89.4	–	0.6	8.5
27	**17**	H_2O_2	20.3	1.3	90.2	–	0.5	8.0
28	**18**	H_2O_2	14.2	1.7	87.7	–	0.9	9.7
29	**19**	H_2O_2	15.4	2.0	85.1	–	0.6	12.3
30	**20**	H_2O_2	14.8	2.2	84.2	–	0.7	12.9
31	**11**	TBHP	78.9	41.0	54.2	2.1	1.0	1.7
32	**12**	TBHP	85.2	41.4	53.6	2.3	1.2	1.5
33	**13**	TBHP	86.3	39.5	55.8	2.0	1.1	1.6
34	**14**	TBHP	83.4	38.8	56.3	2.3	1.2	1.4
35	**15**	TBHP	81.3	36.7	58.6	2.2	1.2	1.3
36	**16**	TBHP	79.1	38.4	56.7	2.3	1.1	1.5
37	**17**	TBHP	85.7	42.3	53.1	2.0	1.0	1.6
38	**18**	TBHP	72.3	46.3	48.4	2.2	1.7	1.4
39	**19**	TBHP	71.7	45.6	49.1	2.4	1.4	1.5
40	**20**	TBHP	70.5	47.8	46.6	2.6	1.2	1.8

[a] Styrene oxide.
[b] Benzaldehyde.
[c] Benzoic acid.
[d] Phenylacetaldehyde.
[e] 1-Phenylethane-1,2-diol.



11: $R^1=R^2=R^3=R^4=R^5=H$
12: $R^2=R^3=R^4=R^5=H$, $R^1=OCH_3$
13: $R^1=R^2=R^4=R^5=H$, $R^3=OCH_3$
14: $R^1=R^3=R^5=H$, $R^2=R^4=OCH_3$
15: $R^1=R^2=R^4=R^5=H$, $R^3=CH_3$
16: $R^1=R^2=R^4=R^5=H$, $R^3=Br$
17: $R^1=R^2=R^5=H$, $R^3\text{-}C_4H_4\text{-}R^4$
18: $R^1=R^2=R^3=R^4=H$, $R^5=CH_3$
19: $R^1=R^2=R^3=R^4=H$, $R^5=C_6H_5$
20: $R^3=R^4=H$, $R^5=CH_3$, $R^1\text{-}C_4H_4\text{-}R^2$

Fig. 6. Structural formulae of vanadium(V) complexes containing ONN-tridentate donor ligands.

the other dioxidovanadium(V) complexes (20–35% conversion) reported earlier [18a]. On the other hand, the selectivity is very similar, with about 50% toward benzaldehyde and about 40% toward styrene oxide. When aqueous 30% H_2O_2 is employed as oxidant, distinctly the lowest conversion of styrene has been observed (≥20%), but as in the case of **1**–**10**, benzaldehyde is the main product (82.4–90.2%). Moreover, as well as for reported earlier dioxidovanadium(V) complexes [18a], styrene oxide is the most expected product but its selectivity goes down considerably (>4%). 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. Very 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 (*ca.* 10%). Formation of other products, *e.g.* phenylacetaldehyde through isomerization of styrene oxide and benzoic acid through oxidation of benzaldehyde, are distinctly much slower processes.

4. Conclusion

Ten new chiral vanadium(V) complexes derived from Schiff base ligands, monocondensation products of *o*-hydroxycarbonyl compounds with R(−)-1-amino-2-propanol were synthesized and characterized by IR, CD, UV–Vis, 1D (^{1}H, ^{51}V) and 2D (COSY, gHSQC) NMR. Moreover, their catalytic properties toward the oxidation of sulfides and styrene, using different oxidants were tested. For comparison, very similar dioxidovanadium(V) complexes but with ONN-type tridentate Schiff bases derived from R(−)-1,2-diaminopropane in the oxidation of styrene have been tested.

In presented sulfoxidation reactions enantioselectivity of vanadium(V) complexes is better and the reaction times are much shorter than for other vanadium(V) complexes with Schiff bases derived from optically active diamines. The results show that the observed yield and enantiomeric excess significantly depend on the nature of the catalyst, substrate and peroxide used, especially in the aspect of bulky substituent leading to large steric demand, and finally depend on the temperature in which the reaction is carried out.

In addition, to test the catalytic potential of the prepared vanadium(V) complexes in the oxidation of olefines, the oxidation of styrene was chosen as the model reaction. These complexes are able to catalyze the oxidative conversion of styrene, by 30% H_2O_2 or TBHP as oxidant, to styrene oxide and successive products derived from styrene oxide, but according to our studies, no clear trend of different catalytic reactivity was found upon the change of substituent in the salicydene part of the Schiff base ligand. The oxidation of styrene after 6 h of reaction time gives at least five different products. Using 30% H_2O_2 as oxidant conversion of styrene was distinctly low, but due to the strong oxidizing nature of H_2O_2 the formation of benzaldehyde was preferred, whereas expected product styrene oxide was found only in small yield. Presence of large amount of water in the reaction mixture may be responsible for the lowering of the % conversion. On the other hand, *tert*-butyl hydroperoxide (TBHP) proved to be an excellent oxidant giving even 99.2% conversion of styrene with benzaldehyde as the main product.

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