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Five- and six-coordinate vanadium(V) complexes with tridentate Schiff base ligands derived from *S*(+)-isoleucinol: Synthesis, characterization and catalytic activity in the oxidation of sulfides and olefins

Grzegorz Romanowski *, Jaromir Kira, Michał Wera

Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, PL-80952 Gdańsk, Poland

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ABSTRACT

A series of vanadium(V) complexes with chiral tridentate Schiff base ligands, obtained by a single condensation of *S*(+)-isoleucinol with salicylaldehyde and its derivatives, and also six-coordinate complexes with additional monoanionic bidentate benzohydroxamate co-ligand, were prepared. The complexes were characterized by elemental analysis and by their IR, CD, UV–Vis, one- (^{1}H, ^{51}V) and two-dimensional (COSY, gHSQC and NOESY) NMR spectra. The X-ray analysis of the complex, (benzohydroxamato-κ^2O,O'){*S*(+)-2-[(1-oxido-3-methylpentyl)iminomethyl]phenolato-κ^3N,O,O'}oxidovanadium(V), 1b, revealed a distorted octahedral VO(ONO)(OO) geometry. The five-coordinate vanadium(V) complexes have ability to catalyze the oxidation of sulfides [PhSR (R = Me, Bz)] using aqueous 30% H_2O_2 in good yields and enantiomeric excesses. Catalytic activity of these complexes were also tested in the oxidation of styrene and cyclohexene, using aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as oxidant.

1. Introduction

The growing interest in recent years in the coordination chemistry of vanadium is generated by the wide range of biological and catalytic properties of particular importance in the biosphere. Five- and six-coordinated vanadium complexes, also with hydroxamic acids as ligands, possess potential medicinal applications, such as the treatment of diabetes type I and II [1], preventive activity against carcinogenesis [2] or exert anti-parasitic effects against American trypanosomiasis, human African trypanosomiasis and leishmaniasis [3]. On the other hand, vanadium nitrogenase in *Azotobacter* genus [4], vanadium-dependent haloperoxidases in marine algae or terrestrial fungi and lichen [5–7], or amavadin in the mushroom *Amanita muscaria* [8], are only few examples of vanadium complexes which can be found in nature.

Optically active sulfoxides possess a wide range of biological activities, *e.g.* antimicrobial properties [9], inhibition of biosynthesis of uric acid [10] and gastric acid secretion [11] or regulation of cholesterol catabolism [12]. As efficient chiral auxiliaries they lead to many important asymmetric transformations [13] and are valuable starting materials in asymmetric synthesis as well as important chiral ligands in enantioselective catalysis. Since epoxides are key starting materials for a wide variety of products the epoxidation of alkenes is one of the most widely studied reactions in organic chemistry. Their importance arises mainly from the ring opening of epoxides, which allows straightforward elaboration to useful generation of new carbon–carbon bonds [14].

Chiral Schiff base ligands are considered "privileged ligands" [15], which can be readily synthesized from chiral aldehydes or chiral amines, and are able to transmit chiral information to produce enantioselectively a number of different products through a catalytic process. Moreover, chiral N-salicyl-β-amino alcohol Schiff bases can be readily synthesized from naturally available chiral amino acids [16] and have been widely employed as catalysts, *i.e.* in the stereoselective synthesis of cyclic ethers [17], the asymmetric alkynylation of aldehydes [18], the epoxidation of cyclooctene [19], the oxidation of bromide [17], oxidative kinetic resolution of α-hydroxy esters [20] or the enantioselective oxidation of organic sulfides [18,21] and trimethylsilylcyanations [22].

In continuation of our studies on synthesis, structure, spectroscopic and catalytic properties of vanadium(V) complexes incorporating chiral tridentate Schiff base ligands [23–26], we prepared a series of new five-coordinate oxidovanadium(V) complexes with ONO donor Schiff base ligands, products of monocondensation of *S*(+)-isoleucinol with aromatic *o*-hydroxyaldehydes, and also six-coordinate with additional monoanionic bidentate benzohydroxamate co-ligand, 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 asymmetric oxidation, *i.e.* enantioselective sulfoxidation of methyl phenyl sulfide (PhSMe) and benzyl phenyl sulfide (PhSBz) by aqueous 30% H_2O_2 has been

* Corresponding author. Tel.: +48 585235102.
E-mail address: greg@chem.univ.gda.pl (G. Romanowski).

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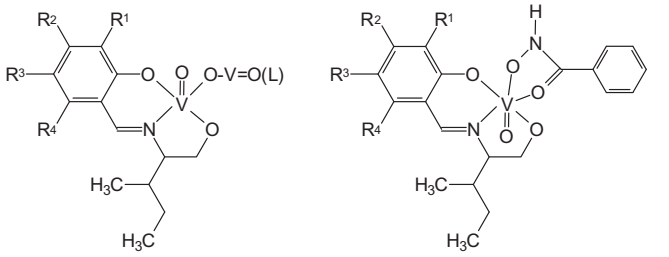

	R1	R2	R3	R4
1	H	H	H	H
2	OCH_3	H	H	H
3	H	H	OCH_3	H
4	H	OCH_3	H	OCH_3

	R1	R2	R3	R4
5	H	H	CH_3	H
6	H	H	Br	H
7	H	H	NO_2	H
8	H	OH	H	H

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

studied. Moreover, they were also used as catalysts in the oxidation of olefins, *i.e.* styrene and cyclohexene, using aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as oxidant. Crystal and molecular structure of the complex, (benzohydroxamato-κ^2*O*,*O*′){*S*(+)-2-[(1-oxido-3-methylpentyl)iminomethyl]phenolato-κ^3*N*,*O*,*O*′}oxidovanadium(V), **1b**, is also reported.

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 CD_3OD solutions with a Varian Mercury-400BB (400 MHz) spectrometer using TMS (^{1}H) 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. X-ray investigations

Diffraction measurements were made on a Oxford Diffraction Gemini R Ultra Ruby CCD, using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 295(2) K and determination of the crystal class, orientation matrix, and accurate unit cell parameters was performed according to established procedures. Data collection and processing parameters are summarized in Table 1. The structure was solved by direct methods and refined with all data on F^2 with SHELXTL [27]. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and treated as riding atoms with fixed thermal parameters.

2.3. Catalytic activity

2.3.1. 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 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 analysed (yield and ee value) by ^{1}H NMR spectra in the presence of chiral shift reagent Eu(hfc)$_3$ (where Hhfc is 3-(heptafluoropropylhydroxymethylene)-(+)-camphoric acid) [28].

2.3.2. Oxidation of olefins

In typical procedure, styrene or cyclohexene (1.00 mmol), an oxidant (3.00 mmol), *i.e.* aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) in decane, and catalyst (0.010 mmol) were taken in CH_3CN (10 ml) and the reaction was carried out for 6 h at 80 °C. 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.

2.4. Complexes

The complexes were obtained in a following example procedure. A solution of 5 mmol of *S*(+)-isoleucinol in absolute ethanol (10 ml) 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) in absolute EtOH (20 ml) and heated under reflux for 1 h. In case of **1b**–**8b**, benzohydroxamic acid (5 mmol) in absolute EtOH (10 ml) was also added with an aldehyde. Then a vanadium(V) oxytriethoxide (5 mmol) in absolute EtOH (10 ml) 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.

Table 1
Crystal data and structure refinement.

Compound	**1b**
Empirical formula	$C_{20}H_{23}N_2O_5V$
Formula weight	422.34
T (K)	295(2)
λ (Å)	0.71073
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	9.0724(4)
b (Å)	10.2624(7)
c (Å)	21.3738(11)
V (Å^3)	1990.00(19)
Z	4
D_{calc} (g cm^{-3})	1.410
Absorption coefficient (mm^{-1})	0.532
F(000)	880
Crystal size (mm)	0.3 × 0.2 × 0.05
θ Range for data collection (°)	2.95 to 25.05
Limiting indices	$-10 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 11$, $-25 \leqslant l \leqslant 23$
Reflections collected/unique	16574/3520 [R_{int} = 0.0808]
Completeness to 2θ (%)	99.8
Data/restraints/parameters	3520/0/269
Goodness-of-fit (GOF) on F^2	0.744
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0345, wR_2 = 0.0405
R indices (all data)	R_1 = 0.1039, wR_2 = 0.0470
Absolute structure parameter	0.01(2)
Largest difference in peak and hole (e Å^{-3})	0.178 and −0.181

*2.4.1. μ-Oxido-bis({S(+)-2-[(1-oxido-3-methylpentyl)iminomethyl] phenolato-κ³N,O,O′}oxidovanadium(V)) (**1a**)*

Yield 73%. *Anal.* Calc. for $C_{26}H_{34}N_2O_7V_2$: C, 53.1; H, 5.8; N, 4.8. Found: C, 53.0; H, 5.7; N, 4.7%. IR (KBr, cm^{-1}): 1623 ($\nu_{C=N}$); 974 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 277 (10320), 328 (4370). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 251 (−3.18), 280 (2.37), 347 (−6.15). ^{1}H NMR (CD_3-OD, ppm) major (60%): 8.64 (1H, s) (azomethine); 7.62–7.52 (2H, m), 7.01–6.92 (2H, m) (aromatic); 4.80 (2H, br s), 1.49 (1H, m), 1.13 (1H, m) (methylene); 3.85 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 2.51 (1H, m) (methine); 1.11 (3H, d, ^3J = 8 Hz), 0.95 (3H, t, ^3J = 8 Hz) (methyl); minor (40%): 8.76 (1H, s) (azomethine); 7.62–7.52 (2H, ov), 7.01–6.92 (2H, ov) (aromatic); 5.02 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 4.68 (1H, br s), 1.41 (1H, m), 1.18 (1H, ov) (methylene); 4.25 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 1.76 (1H, m) (methine); 1.10 (3H, ov), 0.92 (3H, t, ^3J = 8 Hz) (methyl). ^{51}V NMR (CD_3OD, ppm): major (60%): −530.9; minor (40%): −533.8.

*2.4.2. μ-Oxido-bis({S(+)-2-[(1-oxido-3-methylpentyl)iminomethyl]-6-methoxyphenolato-κ³N,O,O′}oxidovanadium(V)) (**2a**)*

Yield 77%. *Anal.* Calc. for $C_{28}H_{38}N_2O_9V_2$: C, 51.9; H, 5.9; N, 4.3. Found: C, 51.7; H, 5.8; N, 4.4%. IR (KBr, cm^{-1}): 1625 ($\nu_{C=N}$); 981 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 285 (10270), 351 (4420). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 252 (−3.89), 278 (2.04) 358 (−4.32). ^{1}H NMR (CD_3-OD, ppm) major (60%): 8.65 (1H, s) (azomethine); 7.23–7.16 (2H, m), 6.96 (1H, d, ^3J = 8 Hz) (aromatic); 4.79 (2H, br s), 1.48 (1H, m), 1.16 (1H, m) (methylene); 3.86 (1H, ov), 2.50 (1H, m) (methine); 1.10 (3H, d, ^3J = 8 Hz), 0.94 (3H, t, ^3J = 8 Hz) (methyl); 3.86 (3H, s) (methoxy); minor (40%): 8.77 (1H, s) (azomethine); 7.23–7.16 (2H, ov), 6.95 (1H, ov) (aromatic); 5.00 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 4.68 (1H, br s), 1.40 (1H, m), 1.17 (1H, ov) (methylene); 4.25 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 1.75 (1H, m) (methine); 1.09 (3H, ov), 0.90 (3H, t, ^3J = 8 Hz) (methyl); 3.88 (3H, s) (methoxy). ^{51}V NMR (CD_3OD, ppm): major (60%): −527.3; minor (40%): −530.7.

*2.4.3. μ-Oxido-bis({S(+)-2-[(1-oxido-3-methylpentyl)iminomethyl]-4-methoxyphenolato-κ³N,O,O′}oxidovanadium(V)) (**3a**)*

Yield 71%. *Anal.* Calc. for $C_{28}H_{38}N_2O_9V_2$: C, 51.9; H, 5.9; N, 4.3. Found: C, 51.8; H, 5.8; N, 4.3%. IR (KBr, cm^{-1}): 1631 ($\nu_{C=N}$); 977 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 284 (9930), 349 (4120). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 253 (−3.05), 280 (2.13), 362 (−4.55). ^{1}H NMR (CD_3-OD, ppm) major (60%): 8.65 (1H, s) (azomethine); 7.22–7.12 (2H, m), 6.89 (1H, d, ^3J = 8 Hz) (aromatic); 4.79 (2H, br s), 1.47 (1H, m), 1.16 (1H, m) (methylene); 3.84 (1H, ov), 2.52 (1H, m) (methine); 1.12 (3H, d, ^3J = 8 Hz), 0.96 (3H, t, ^3J = 8 Hz) (methyl); 3.83 (3H, s) (methoxy); minor (40%): 8.76 (1H, s) (azomethine); 7.22–7.12 (2H, ov), 6.95 (1H, d, ^3J = 8 Hz) (aromatic); 4.99 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 4.67 (1H, br s), 1.42 (1H, m), 1.18 (1H, ov) (methylene); 4.27 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 1.75 (1H, m) (methine); 1.10 (3H, ov), 0.91 (3H, t, ^3J = 8 Hz) (methyl); 3.85 (3H, s) (methoxy). ^{51}V NMR (CD_3OD, ppm): major (60%): −525.9; minor (40%): −530.6.

*2.4.4. μ-Oxido-bis({S(+)-2-[(1-oxido-3-methylpentyl)iminomethyl]-3,5-dimethoxyphenolato-κ³N,O,O′}oxidovanadium(V)) (**4a**)*

Yield 74%. *Anal.* Calc. for $C_{30}H_{42}N_2O_{11}V_2$: C, 50.9; H, 6.0; N, 4.0. Found: C, 51.0; H, 6.1; N, 4.0%. IR (KBr, cm^{-1}): 1628 ($\nu_{C=N}$); 986 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 317 (20180). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 251 (−2.91), 283 (2.03), 348 (−3.62). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.67 (1H, s) (azomethine); 6.33 (1H, d, ^4J = 3 Hz), 6.26 (1H, d, ^4J = 3 Hz) (aromatic); 4.77 (2H, br s), 1.46 (1H, m), 1.15 (1H, m) (methylene); 3.82 (1H, ov), 2.50 (1H, m) (methine); 1.11 (3H, d, ^3J = 8 Hz), 0.95 (3H, t, ^3J = 8 Hz) (methyl); 3.89 (3H, s), 3.85 (3H, s) (methoxy); minor (40%): 8.85 (1H, s) (azomethine); 6.31 (1H, ov), 6.24 (1H, ov) (aromatic); 4.97 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 4.66 (1H, br s), 1.40 (1H, m), 1.16 (1H, ov) (methylene); 4.25 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 1.74 (1H, m) (methine); 1.09 (3H, ov), 0.90 (3H, t, ^3J = 8 Hz) (methyl); 3.90 (3H, ov), 3.86 (3H, ov) (methoxy). ^{51}V NMR (CD_3OD, ppm) major (60%): −526.5, minor (40%): −530.2.

*2.4.5. μ-Oxido-bis({S(+)-2-[(1-oxido-3-methylpentyl)iminomethyl]-4-methylphenolato-κ³N,O,O′}oxidovanadium(V)) (**5a**)*

Yield 72%. *Anal.* Calc. for $C_{28}H_{38}N_2O_7V_2$: C, 54.6; H, 6.2; N, 4.5. Found: C, 54.5; H, 6.1; N, 4.5%. IR (KBr, cm^{-1}): 1626 ($\nu_{C=N}$); 978 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 282 (9910), 349 (4050). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 252 (−3.89), 293 (3.18), 356 (−6.47). ^{1}H NMR (CD_3-OD, ppm) major (60%): 8.60 (1H, s) (azomethine); 7.40–7.36 (2H, m), 6.84 (1H, d, ^3J = 8 Hz) (aromatic); 4.79 (2H, br s), 1.48 (1H, m), 1.14 (1H, m) (methylene); 3.83 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 2.51 (1H, m) (methine); 2.34 (3H, s), 1.10 (3H, d, ^3J = 8 Hz), 0.94 (3H, t, ^3J = 8 Hz) (methyl); minor (40%): 8.72 (1H, s) (azomethine); 7.40–7.36 (2H, ov), 6.90 (1H, d, ^3J = 8 Hz) (aromatic); 5.01 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 4.66 (1H, br s), 1.40 (1H, m), 1.16 (1H, ov) (methylene); 4.23 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 1.73 (1H, m) (methine); 2.36 (3H, s), 1.09 (3H, ov), 0.91 (3H, ov) (methyl). ^{51}V NMR (CD_3OD, ppm): major (60%): −528.0; minor (40%): −531.8.

*2.4.6. μ-Oxido-bis({S(+)-2-[(1-oxido-3-methylpentyl)iminomethyl]-4-bromophenolato-κ³N,O,O′}oxidovanadium(V)) (**6a**)*

Yield 77%. *Anal.* Calc. for $Br_2C_{26}H_{32}N_2O_7V_2$: C, 41.8; H, 4.3; N, 3.8. Found: C, 41.7; H, 4.2; N, 3.9%. IR (KBr, cm^{-1}): 1627 ($\nu_{C=N}$); 978 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 280 (10620), 347 (4520). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 255 (−2.76), 283 (1.84), 352 (−4.23). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.58 (1H, s) (azomethine); 7.71 (1H, d, ^3J = 3 Hz), 7.60 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 6.85 (1H, d, ^3J = 8 Hz) (aromatic); 4.75 (2H, br s), 1.49 (1H, m), 1.15 (1H, m) (methylene); 3.86 (1H, ov), 2.48 (1H, m) (methine); 1.09 (3H, d, ^3J = 8 Hz), 0.94 (3H, t, ^3J = 8 Hz) (methyl); minor (40%): 8.69 (1H, s) (azomethine); 7.74 (1H, d, ^3J = 3 Hz), 7.61 (1H, ov), 6.90 (1H, d, ^3J = 8 Hz) (aromatic); 5.00 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 4.65 (1H, br s), 1.38 (1H, m), 1.16 (1H, ov) (methylene); 4.18 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 1.79 (1H, m) (methine); 1.10 (3H, ov), 0.92 (3H, ov) (methyl). ^{51}V NMR (CD_3OD, ppm) major (60%): −531.1, minor (40%): −532.8.

*2.4.7. μ-Oxido-bis({S(+)-2-[(1-oxido-3-methylpentyl)iminomethyl]-4-nitrophenolato-κ³N,O,O′}oxidovanadium(V)) (**7a**)*

Yield 72%. *Anal.* Calc. for $C_{26}H_{32}N_4O_{11}V_2$: C, 46.0; H, 4.8; N, 8.3. Found: C, 46.1; H, 4.9; N, 8.3. IR (KBr, cm^{-1}): 1636 ($\nu_{C=N}$); 1557, 1332 (ν_{NO_2}); 986 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 345 (15910). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 254 (−3.18), 309 (2.48), 348 (−4.95). ^{1}H NMR (CD_3-OD, ppm) major (60%): 8.70 (1H, s) (azomethine); 8.56 (1H, d, ^4J = 3 Hz), 8.34 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 6.96 (1H, d, ^3J = 8 Hz) (aromatic); 5.00 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 4.77 (1H, br s), 1.49 (1H, m), 1.22 (1H, m) (methylene); 3.98 (1H, m), 2.48 (1H, m) (methine); 1.10 (3H, d, ^3J = 8 Hz), 0.99 (3H, t, ^3J = 8 Hz) (methyl); minor (40%): 8.77 (1H, s) (azomethine); 8.71 (1H, ov), 8.57 (1H, ov), 7.04 (1H, d, ^3J = 8 Hz) (aromatic); 5.10 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 4.67 (1H, ov), 1.36 (1H, m), 1.06 (1H, ov) (methylene); 4.11 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 1.85 (1H, m) (methine); 1.09 (3H, ov), 0.97 (3H, ov) (methyl). ^{51}V NMR (CD_3OD, ppm) major (60%): −529.6, minor (40%): −528.9.

*2.4.8. μ-Oxido-bis({S(+)-2-[(1-oxido-3-methylpentyl)iminomethyl]-5-hydroxyphenolato-κ^3N,O,O′}oxidovanadium(V)) (**8a**)*

Yield 76%. *Anal.* Calc. for $C_{26}H_{34}N_2O_9V_2$: C, 50.3; H, 5.5; N, 4.5. Found: C, 50.5; H, 5.6; N, 4.4%. IR (KBr, cm^{-1}): 1618 ($\nu_{C=N}$); 956 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 288 (11170), 355 (4730). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 251 (−3.85), 278 (3.64), 354 (−6.96). ^{1}H NMR (CD_3-OD, ppm) major (60%): 8.46 (1H, s) (azomethine); 7.38 (1H, d, ^3J = 8 Hz), 6.44 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 6.31 (1H, d, ^4J = 3 Hz) (aromatic); 4.78 (2H, br s), 1.48 (1H, m), 1.15 (1H, m) (methylene); 3.79 (1H, m), 2.47 (1H, m) (methine); 1.09 (3H, d, ^3J = 8 Hz), 0.92 (3H, t, ^3J = 8 Hz) (methyl); minor (40%): 8.60 (1H, s) (azomethine); 7.43 (1H, d, ^3J = 8 Hz), 6.48 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 6.38 (1H, d, ^4J = 3 Hz) (aromatic); 5.00 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 4.63 (1H, br s), 1.39 (1H, m), 1.11 (1H, ov) (methylene); 4.22 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 1.71 (1H, m) (methine); 1.08 (3H, ov), 0.88 (3H, ov) (methyl). ^{51}V NMR (CD_3OD, ppm) major (60%): −526.3, minor (40%): −530.0.

*2.4.9. (Benzohydroxamato-κ^2O,O′){S(+)-2-[(1-oxido-3-methylpentyl) iminomethyl]phenolato-κ^3N,O,O′}oxidovanadium(V) (**1b**)*

Yield 81%. *Anal.* Calc. for $C_{20}H_{23}N_2O_5V$: C, 56.9; H, 5.5; N, 6.6. Found: C, 57.0; H, 5.6; N, 6.7%. IR (KBr, cm^{-1}): 3448 (ν_{N-H}); 1626, 1602 ($\nu_{C=O,}$ $\nu_{C=N}$); 965 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 258 (12530), 463 (3640). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 269 (−3.99), 296 (−2.84), 356 (−4.81), 510 (2.21). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.78 (1H, s) (azomethine); 7.84 (1H, d, ^3J = 8 Hz), 7.67–7.32 (5H, m), 7.01–6.90 (2H, m), 6.77 (1H, d, ^3J = 8 Hz) (aromatic); 4.70 (1H, d, ^3J = 8 Hz), 4.61 (1H, dd, ^3J = 8 Hz, ^4J = 4 Hz), 1.49 (1H, m), 1.13 (1H, m) (methylene); 4.02 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 2.48 (1H, m) (methine); 1.11 (3H, d, ^3J = 8 Hz), 0.95 (3H, t, ^3J = 8 Hz) (methyl); minor (40%): 8.82 (1H, s) (azomethine); 7.79 (1H, d, ^3J = 8 Hz), 7.67–7.32 (5H, ov), 7.01–6.90 (2H, ov), 6.86 (1H, d, ^3J = 8 Hz) (aromatic); 4.92 (1H, ov), 4.79 (1H, d, ^3J = 8 Hz), 1.41 (1H, m), 1.18 (1H, ov) (methylene); 4.22 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 2.05 (1H, m) (methine); 1.10 (3H, ov), 0.92 (3H, t, ^3J = 8 Hz) (methyl). ^{51}V NMR (CD_3OD, ppm): major (60%): −457.7; minor (40%): −451.4.

*2.4.10. (Benzohydroxamato-κ^2O,O′){S(+)-2-[(1-oxido-3-methylpentyl) iminomethyl]-6-methoxyphenolato-κ^3N,O,O′}oxidovanadium(V) (**2b**)*

Yield 83%. *Anal.* Calc. for $C_{21}H_{25}N_2O_6V$: C, 55.8; H, 5.6; N, 6.2. Found: C, 55.7; H, 5.5; N, 6.1%. IR (KBr, cm^{-1}): 3436 (ν_{N-H}); 1621, 1598 ($\nu_{C=O,}$ $\nu_{C=N}$); 961 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 261 (12870), 486 (3920). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 275 (−4.15), 313 (3.46), 368 (−3.39), 517 (3.18). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.78 (1H, s) (azomethine); 7.84 (1H, d, ^3J = 8 Hz), 7.57–7.46 (3H, m), 7.37 (1H, d, ^3J = 8 Hz), 7.21 (1H, d, ^3J = 8 Hz), 7.12 (1H, d, ^3J = 8 Hz), 6.76 (1H, d, ^3J = 8 Hz) (aromatic); 4.72 (1H, d, ^3J = 8 Hz), 4.59 (1H, dd, ^3J = 8 Hz, ^4J = 4 Hz), 1.51 (1H, m), 1.17 (1H, m) (methylene); 4.06 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 2.47 (1H, m) (methine); 1.13 (3H, d, ^3J = 8 Hz), 0.95 (3H, t, ^3J = 8 Hz) (methyl); 3.86 (3H, s) (methoxy); minor (40%): 8.82 (1H, s) (azomethine); 7.78 (1H, d, ^3J = 8 Hz), 7.59–7.50 (3H, ov), 7.35 (1H, ov), 7.19 (1H, ov), 7.10 (3H, ov), 6.89 (1H, d, ^3J = 8 Hz) (aromatic); 4.97 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 4.81 (1H, d, ^3J = 8 Hz), 1.47 (1H, ov), 1.14 (1H, ov) (methylene); 4.20 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 2.04 (1H, m) (methine); 1.10 (3H, ov), 0.97 (3H, t, ^3J = 8 Hz) (methyl); 3.85 (3H, s) (methoxy). ^{51}V NMR (CD_3OD, ppm): major (60%): −451.7; minor (40%): −446.0.

*2.4.11. (Benzohydroxamato-κ^2O,O′){S(+)-2-[(1-oxido-3-methylpentyl) iminomethyl]-4-methoxyphenolato-κ^3N,O,O′}oxidovanadium(V) (**3b**)*

Yield 78%. *Anal.* Calc. for $C_{21}H_{25}N_2O_6V$: C, 55.8; H, 5.6; N, 6.2. Found: C, 55.6; H, 5.5; N, 6.2%. IR (KBr, cm^{-1}): 3433 (ν_{N-H}); 1628, 1605 ($\nu_{C=O,}$ $\nu_{C=N}$); 966 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 259 (13040), 484 (4080). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 273 (−4.42), 311 (2.57), 381 (−4.14), 519 (2.42). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.78 (1H, s) (azomethine); 7.83 (1H, d, ^3J = 8 Hz), 7.57–7.37 (3H, m), 7.23–7.10 (3H, m), 6.70 (1H, d, ^3J = 8 Hz) (aromatic); 4.71 (1H, d, ^3J = 8 Hz), 4.58 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 1.51 (1H, m), 1.16 (1H, m) (methylene); 4.01 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 2.49 (1H, m) (methine); 1.12 (3H, d, ^3J = 8 Hz), 0.96 (3H, t, ^3J = 8 Hz) (methyl); 3.83 (3H, s) (methoxy); minor (40%): 8.81 (1H, s) (azomethine); 7.79 (1H, d, ^3J = 8 Hz), 7.57–7.37 (3H, ov), 7.23–7.10 (3H, ov), 6.88 (1H, d, ^3J = 8 Hz) (aromatic); 4.98 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 4.79 (1H, d, ^3J = 8 Hz), 1.42 (1H, m), 1.18 (1H, ov) (methylene); 4.18 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 2.04 (1H, m) (methine); 1.10 (3H, ov), 0.91 (3H, t, ^3J = 8 Hz) (methyl); 3.85 (3H, s) (methoxy). ^{51}V NMR (CD_3OD, ppm): major (60%): −453.8; minor (40%): −450.0.

*2.4.12. (Benzohydroxamato-κ^2O,O′){S(+)-2-[(1-oxido-3-methylpentyl) iminomethyl]-3,5-dimethoxyphenolato-κ^3N,O,O′}oxidovanadium(V) (**4b**)*

Yield 81%. *Anal.* Calc. for $C_{22}H_{27}N_2O_7V$: C, 54.8; H, 5.6; N, 5.8. Found: C, 54.9; H, 5.7; N, 5.7%. IR (KBr, cm^{-1}): 3435 (ν_{N-H}); 1603, 1547 ($\nu_{C=O,}$ $\nu_{C=N}$); 968 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 314 (16350), 487 (4570). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 284 (−5.01), 306 (2.78), 348 (−5.74), 512 (2.31). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.92 (1H, s) (azomethine); 7.82 (1H, d, ^3J = 8 Hz), 7.60–7.37 (5H, m), 6.04 (1H, d, ^4J = 3 Hz), 5.93 (1H, d, ^4J = 3 Hz) (aromatic); 4.66 (1H, d, ^3J = 8 Hz), 4.60 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 1.54 (1H, m), 1.14 (1H, m) (methylene); 4.11 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 2.44 (1H, m) (methine); 1.12 (3H, d, ^3J = 8 Hz), 0.96 (3H, t, ^3J = 8 Hz) (methyl); 3.92 (3H, s), 3.78 (3H, s) (methoxy); minor (40%): 8.96 (1H, s) (azomethine); 7.78 (1H, d, ^3J = 8 Hz), 7.60–7.37 (5H, ov), 6.11 (1H, d, ^4J = 3 Hz), 6.06 (1H, d, ^4J = 3 Hz) (aromatic); 4.99 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 4.78 (1H, d, ^3J = 8 Hz), 1.42 (1H, m), 1.19 (1H, ov) (methylene); 4.27 (1H, dd, ^3J = 8 Hz, ^4J = 6 Hz), 2.03 (1H, m) (methine); 1.11 (3H, ov), 0.92 (3H, t, ^3J = 8 Hz) (methyl); 3.93 (3H, s), 3.79 (3H, s) (methoxy). ^{51}V NMR (CD_3OD, ppm): major (60%): −456.2; minor (40%): −450.8.

*2.4.13. (Benzohydroxamato-κ^2O,O′){S(+)-2-[(1-oxido-3-methylpentyl) iminomethyl]-4-methylphenolato-κ^3N,O,O′}oxidovanadium(V) (**5b**)*

Yield 79%. *Anal.* Calc. for $C_{21}H_{25}N_2O_5V$: C, 57.8; H, 5.8; N, 6.4. Found: C, 57.9; H, 5.9; N, 6.3%. IR (KBr, cm^{-1}): 3435 (ν_{N-H}); 1625, 1590 ($\nu_{C=O,}$ $\nu_{C=N}$); 957 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 266 (12430), 479 (3710). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 271 (−4.92), 299 (2.54), 369 (−4.66), 516 (2.27). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.73 (1H, s) (azomethine); 7.83 (1H, d, ^3J = 8 Hz), 7.60–7.43 (3H, m), 7.40–7.33 (3H, m), 6.67 (1H, d, ^3J = 8 Hz) (aromatic); 4.70 (1H, d, ^3J = 8 Hz), 4.58 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 1.50 (1H, m), 1.14 (1H, m) (methylene); 4.02 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 2.49 (1H, m) (methine); 2.34 (3H, s), 1.10 (3H, d, ^3J = 8 Hz), 0.94 (3H, t, ^3J = 8 Hz) (methyl); minor (40%): 8.77 (1H, s) (azomethine); 7.79 (1H, d, ^3J = 8 Hz), 7.60–7.43 (3H, ov), 7.40–7.33 (2H, ov), 7.30 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 6.84 (1H, d, ^3J = 8 Hz) (aromatic); 4.90 (1H, ov), 4.79 (1H, d, ^3J = 8 Hz), 1.40 (1H, m), 1.16 (1H, ov) (methylene); 4.18 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 2.03 (1H, m) (methine); 2.36 (3H, s), 1.09 (3H, ov), 0.91 (3H, t, ^3J = 8 Hz) (methyl). ^{51}V NMR (CD_3OD, ppm): major (60%): −455.0; minor (40%): −447.8.

*2.4.14. (Benzohydroxamato-κ²O,O′){S(+)-2-[(1-oxido-3-methylpentyl) iminomethyl]-4-bromophenolato-κ³N,O,O′}oxidovanadium(V) (**6b**)*

Yield 82%. *Anal.* Calc. for $BrC_{20}H_{22}N_2O_5V$: C, 47.9; H, 4.4; N, 5.6. Found: C, 47.8; H, 4.5; N, 5.7%. IR (KBr, cm^{-1}): 3443 (ν_{N-H}); 1623, 1598 ($\nu_{C=O,}$ $\nu_{C=N}$); 959 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 264 (12180), 488 (3620). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 271 (−3.58), 309 (2.10), 367 (−4.12), 514 (1.84). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.76 (1H, s) (azomethine); 7.76 (1H, d, ^3J = 3 Hz), 7.57–7.48 (5H, m), 7.41 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 6.69 (1H, d, ^3J = 8 Hz) (aromatic); 4.75 (1H, d, ^3J = 8 Hz), 4.63 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 1.52 (1H, m), 1.15 (1H, m) (methylene); 4.07 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 2.46 (1H, m) (methine); 1.14 (3H, d, ^3J = 8 Hz), 0.97 (3H, t, ^3J = 8 Hz) (methyl); minor (40%): 8.79 (1H, s) (azomethine); 7.81 (1H, d, ^3J = 8 Hz), 7.56–7.47 (5H, ov), 7.62 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 6.83 (1H, d, ^3J = 8 Hz) (aromatic); 4.94 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 4.85 (1H, ov), 1.45 (1H, m), 1.17 (1H, ov) (methylene); 4.22 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 2.04 (1H, m) (methine); 1.11 (3H, ov), 0.95 (3H, t, ^3J = 8 Hz) (methyl). ^{51}V NMR (CD_3OD, ppm): major (60%): −452.5; minor (40%): −443.7.

*2.4.15. (Benzohydroxamato-κ²O,O′){S(+)-2-[(1-oxido-3-methylpentyl) iminomethyl]-4-nitrophenolato-κ³N,O,O′}oxidovanadium(V) (**7b**)*

Yield 76%. *Anal.* Calc. for $C_{20}H_{22}N_3O_7V$: C, 51.4; H, 4.7; N, 9.0. Found: C, 51.3; H, 4.6; N, 9.1%. IR (KBr, cm^{-1}): 3440 (ν_{N-H}); 1636, 1606 ($\nu_{C=O,}$ $\nu_{C=N}$); 1554, 1325 (ν_{NO_2}); 953 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 343 (15270), 480 (4390). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 274 (−4.03), 310 (2.34), 361 (−4.74), 513 (2.06). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.93 (1H, s) (azomethine); 8.63 (1H, d, ^4J = 3 Hz), 8.28 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 7.62–7.50 (5H, m), 6.88 (1H, d, ^3J = 8 Hz) (aromatic); 4.81 (1H, d, ^3J = 8 Hz), 4.74 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 1.54 (1H, m), 1.23 (1H, m) (methylene); 4.14 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 2.52 (1H, m) (methine); 1.17 (3H, d, ^3J = 8 Hz), 0.99 (3H, t, ^3J = 8 Hz) (methyl); minor (40%): 8.95 (1H, s) (azomethine); 8.65 (1H, d, ^3J = 8 Hz), 8.33 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 7.38–7.47 (5H, m), 7.01 (1H, d, ^3J = 8 Hz) (aromatic); 5.13 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 4.97 (1H, d, ^3J = 8 Hz), 1.46 (1H, m), 1.29 (1H, ov) (methylene); 4.31 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 2.08 (1H, m) (methine); 1.15 (3H, ov), 0.97 (3H, t, ^3J = 8 Hz) (methyl). ^{51}V NMR (CD_3OD, ppm): major (60%): −444.7; minor (40%): −431.5.

*2.4.16. (Benzohydroxamato-κ²O,O′){S(+)-2-[(1-oxido-3-methylpentyl) iminomethyl]-5-hydroxyphenolato-κ³N,O,O′}oxidovanadium(V) (**8b**)*

Yield 81%. *Anal.* Calc. for $C_{20}H_{23}N_2O_6V$: C, 54.8; H, 5.3; N, 6.4. Found: C, 54.9; H, 5.4; N, 6.3%. IR (KBr, cm^{-1}): 3438 (ν_{N-H}); 1617, 1587 ($\nu_{C=O,}$ $\nu_{C=N}$); 956 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 265 (12240), 483 (3920). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 270 (−3.76), 306 (2.19), 357 (−4.14), 511 (1.97). ^{1}H NMR (CD_3OD, ppm) major (60%): 8.68 (1H, s) (azomethine); 7.60 (1H, d, ^4J = 3 Hz), 7.56–7.45 (5H, m), 6.65 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 6.53 (1H, d, ^3J = 8 Hz) (aromatic); 4.73 (1H, d, ^3J = 8 Hz), 4.61 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 1.53 (1H, m), 1.19 (1H, m) (methylene); 4.10 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 2.49 (1H, m) (methine); 1.15 (3H, d, ^3J = 8 Hz), 0.98 (3H, t, ^3J = 8 Hz) (methyl); minor (40%): 8.70 (1H, s) (azomethine); 7.63 (1H, d, ^3J = 8 Hz), 7.50–7.39 (5H, ov), 6.69 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 6.57 (1H, d, ^3J = 8 Hz) (aromatic); 4.98 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 4.87 (1H, d, ^3J = 8 Hz), 1.46 (1H, m), 1.17 (1H, ov) (methylene); 4.18 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz), 2.06 (1H, m) (methine); 1.12 (3H, ov), 0.96 (3H, t, ^3J = 8 Hz) (methyl). ^{51}V NMR (CD_3OD, ppm): major (60%): −449.3; minor (40%): −440.6.

3. Results and discussion

3.1. Crystal and molecular structure of **1b**

The crystallographic data of the complex **1b** are summarized in Table 1, and the selected bond distances and angles are given in Table 2.

The complex 1b crystallizes in the orthorhombic system, space group $P2_12_12_1$ with four molecules in the asymmetric unit. The vanadium atom is six-coordinated by one oxido group, two oxygen atoms and one nitrogen atom of the tridentate Schiff base ligand, and by two oxygen atoms of the *O,O′*-bidentate hydroxamate co-ligand, defining a distorted octahedral VO(ONO)(OO) geometry (Fig. 2). The equatorial plane is defined by one nitrogen atom (N8) and two oxygen atoms (O15 and O17) of the tridentate Schiff base ligand and the oxime oxygen atom (O19) of the acetohydroxamate co-ligand, while the oxido oxygen atom (O18) and oxygen carbonyl atom (O22) of the hydroxamate group occupy axial positions. The vanadium atom is displaced from the least squares equatorial plane toward the terminal oxido group by 0.265 Å. In *trans* position to the terminal oxido group is the O22 atom of the acetohydroxamate co-ligand with the bond distance from vanadium atom of 2.197(2) Å that is significantly longer than V16–O19(oxime) bond distance (1.894(2) Å), due to this strong *trans* influence [29]. Also, the *trans* angle is 169.66(11)° and these values correspond well with 2.164(2), 1.856(2) Å distances and 169.3(1)° angle for [V^VO(sal-gly)(bz)] reported earlier [30]. Moreover, the V16 = O18 distance of 1.5977(18) Å and also, the values for V16–O17(phenolate) and V16–N8(imine) bonds being 1.874(2) and 2.104(3) Å, respectively, are in the range found in other similar vanadium(V) complexes with hydroxamate co-ligands [30–34].

The tridentate Schiff base ligand and the benzohydroxamate co-ligand combine with the vanadium atom to give one six-membered and two five-membered chelate rings. The Schiff base five-membered chelate ring containing V16, O15, C14, C9 and N8 atoms adopts an envelope conformation on C14 atom with P = 240.6(2)° and Tau(M) = 51.6(2)° for reference bond V16–O15 [35], whereas the five-membered chelate ring, involving V16,

Table 2
Selected bond lengths (Å), angles (°) and hydrogen bonding parameters (Å, °) for **1b**.

V16–O18	1.5977(18)	O18–V16–O17	95.68(12)
V16–O17	1.874(2)	O18–V16–O19	93.71(10)
V16–N8	2.104(3)	O18–V16–O22	169.66(11)
V16–O15	1.873(2)	O18–V16–N8	106.15(10)
V16–O19	1.894(2)	O18–V16–O15	97.51(11)
V16–O22	2.197(2)	O17–V16–O19	96.32(10)
O19–N20	1.353(3)	O17–V16–O22	84.46(11)
O22–C21	1.245(4)	O17–V16–N8	83.86(10)
N20–C21	1.319(4)	O17–V16–O15	160.16(10)
C1–O17	1.314(4)	N8–V16–O19	160.04(10)
C1–C2	1.403(5)	N8–V16–O22	84.16(10)
C2–C7	1.433(5)	N8–V16–O15	78.28(10)
C7–N8	1.279(3)	O15–V16–O19	97.54(9)
		O15–V16–O22	85.20(9)
		O19–V16–O22	76.02(10)

DH···A	D–H	H···A	D···A	DH···A
N20–H20···O15^{i}	1.07(3)	1.82(3)	2.845(3)	161
C3–H3···O18^{ii}	0.93	2.42	3.293(4)	156
C14–H14A···O22	0.97	2.53	3.022(5)	111
C24–H24A···N20	0.93	2.59	2.891(5)	100
C24–H24A···O18^{i}	0.93	2.39	3.110(4)	135
C28–H28A···O22	0.93	2.49	2.800(5)	100
C5–H5···Cg2^{iii}	0.93	2.71	3.552(5)	152
C9–H9···Cg1^{ii}	0.98	2.83	3.728(4)	152
C13–H13···Cg1^{iv}	0.96	2.34	3.238(7)	156

Symmetry code: (*i*) −*x* + 1, *y* − ½, −*z* + 3/2; (*ii*) *x* − ½, −*y* + 3/2, −*z* + 2; (*iii*) *x* + ½, −*y* + ½, −*z* + 2; (*iv*) *x* + ½, −*y* + 3/2, −*z* + 2.
Notes: Cg1 and Cg2 denotes the centroids of the C1–C6 and C23–C28, respectively.

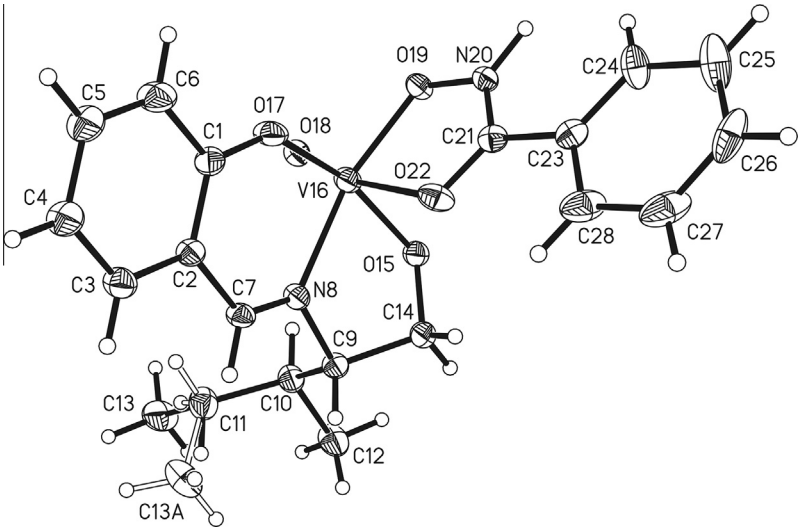

Fig. 2. The molecular structure of **1b**, with displacement ellipsoids drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radius.

O19, N20, C21 and O22 atoms from benzohydroxamate co-ligand, is basically planar. Suprisingly, the six-membered chelate ring, involving V16, O17, C1, C2, C7 and N8 atoms, is also planar.

The loss of only one proton, from acetohydroxamic acid, yielding the hydroxamate anion, not the hydroximate dianion, is revealed by comparison of bond distances and angles between the hydroxamate ring of **1b**, and the hydroximate ring in the vanadium(V) complex, [VO(HSHED)SHI], with hydroximate co-ligand reported earlier [31]. The distance of the N20–C21 bond is comparable, showing its partial double-bond character, but there are significant differences in some of the bond distances in this five-membered chelate ring. The obvious decrease in C21–O22 bond length by 0.029 Å, owing to the stronger partial double-bond character, and increase in V16–O22 bond length by 0.075 Å, owing to the significantly much weaker bond, where oxygen atom has neutral (not negative) charge, are observed. It is also noteworthy to mention that bond between vanadium atom and deprotonated alcoholate oxygen (O15) atom is by 0.292 Å shorter than in [VO(HSHED)SHI] with coordination bond between vanadium and secondary amine nitrogen atoms. In the final stage of anisotropic refinement conformation disorder of *sec*-butyl side chain of β-aminoalcohol moiety was recognized. The disorder of C13 atom with its three hydrogens and also two hydrogens of C11 atom is displayed in Fig. 2. The refined site occupancy values are 0.483(6) for C13 and 0.517(6) for C13A.

The crystal structure of the **1b** complex is stabilized by the intermolecular hydrogen bonds and C–H···O contacts linking the neighboring complex molecules into two-dimensional infinite network, *i.e.* hydrogen bonds between nitrogen oxime atom (N20) of a one molecule and alcoholate oxygen atom (O15) of neighboring molecule and other close contact between C24 carbon atom and oxide group (O18) result in formation of chains extending in the *b* axis direction (Fig. 3). Apart from the intermolecular hydrogen bonds and close contacts these chains are additionally stabilized by C–H···π interactions (Fig. 4).

3.2. Spectroscopic properties

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

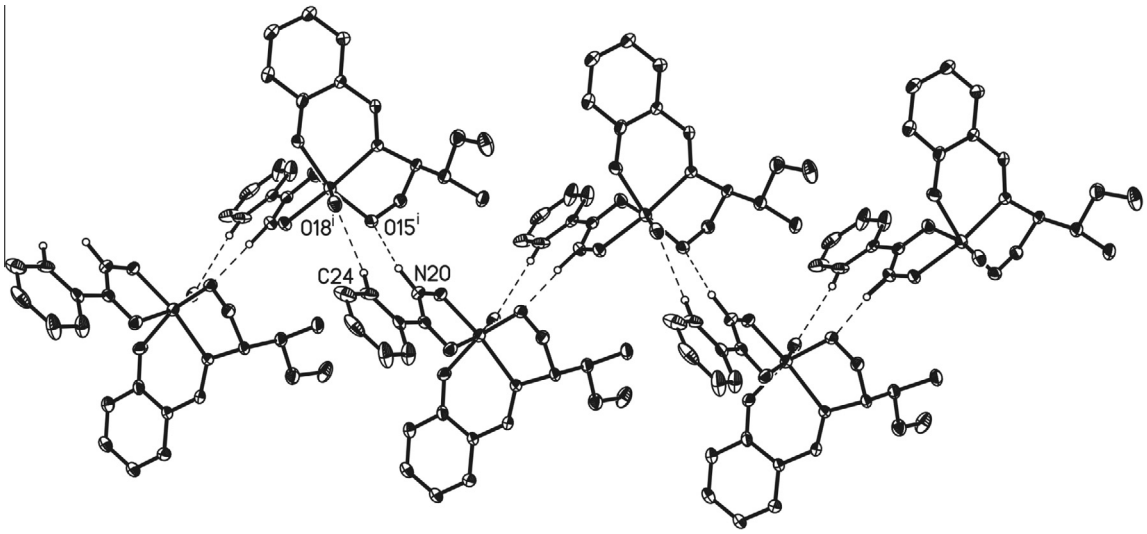

Fig. 3. The arrangement of the molecules of **1b** in the crystal structure. The N–H···O and C–H···O contacts are represented by dashed lines. H atoms not involved in interactions were omitted.

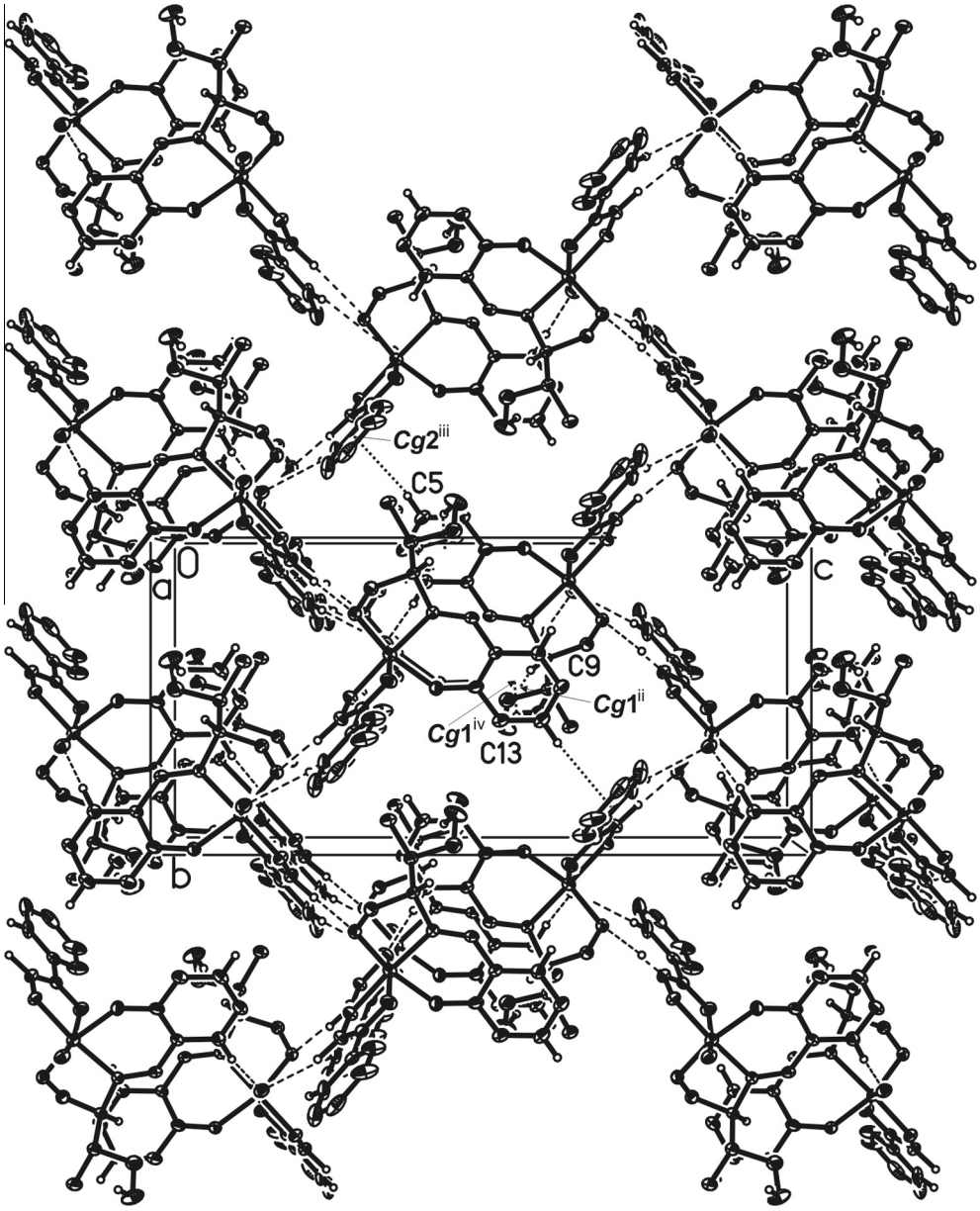

Fig. 4. View of the crystal structure of **1b** approximately along the *a* axis. The C–H···π interactions are represented by dotted lines.

The IR spectra of solid complexes display strong C=N stretch (around 1603–1636 cm^{-1}), additionally associated with the aromatic C=C stretching band, which indicates the C=N group of the coordinated Schiff base ligands [36,37]. A strong band appearing in the 944–986 cm^{-1} region in all the complexes may be attributed to single V=O stretching vibrations, which are close to values reported for related oxidovanadium(V) Schiff base complexes [17,19,25,26]. Additionally, the spectra of **1b**–**8b** complexes exhibit broad strong band in 3433–3448 cm^{-1} ranges, assigned to ν(N–H) stretch of benzohydroxamate co-ligand. The appearance of weak/medium band near 2800 cm^{-1} separate from other C–H stretching vibrations in **2a**–**4a** and **2b**–**4b** complexes indicated the presence of the methoxy substituents [38]. Also, only in the cases of **7a** and **7b** the strong bands appear at 1332, 1557 and 1325, 1554 cm^{-1}, respectively, which are typical for nitro group.

The electronic and circular dichroism spectra of all the complexes were recorded in methanol. Strong intense bands, ε_{max} = 9910–11170 M^{-1} cm^{-1}, with λ_{max} in region 277–288 nm for **1a**–**3a**, **5a**, **6a**, **8a** and in the 258–266 nm range (ε_{max} = 12180–13040 M^{-1} cm^{-1}) for **1b**–**3b**, **5b**, **6b**, **8b** are considered to arise from intraligand π–π^* transitions. The low energy bands, recorded for **1a**–**3a**, **5a**, **6a**, **8a** and **1b**–**8b** complexes, between 328–355 nm (ε_{max} = 4050–4730 M^{-1} cm^{-1}) and 463–488 nm (ε_{max} = 3620–4570 M^{-1} cm^{-1}), respectively, 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 [39]. The spectra of **4a**, **4b**, **7a** and **7b** complexes examined in the same spectral region display very strong bands at 317 (ε_{max} = 20180 M^{-1} cm^{-1}), 314 (ε_{max} = 16350 M^{-1} cm^{-1}), 345 (ε_{max} = 15910 M^{-1} cm^{-1}) and 343 nm (ε_{max} = 15270 M^{-1} cm^{-1}), respectively, similar to the same strong bands at around 320 and 350 nm for the other vanadium(V) complexes derived from 4,6-dimethoxysalicylaldehyde and 5-nitrosalicylaldehyde [24–26]. The circular dichroism spectra of the complexes **1a**–**8a** revealed an additional band in the 251–255 nm range of π–π^* transitions origin. On the other hand, **1b**–**8b** complexes possessing

benzohydroxamate co-ligand, in comparison to their electronic spectra, revealed two additional bands in the 296–313 nm and the 348–381 nm range with the positive and negative Cotton effect, respectively.

In the ^{1}H NMR spectra of all the complexes 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 the complexes, 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% [18]. 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. [40], 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 [41] and disappear when methanol is used as solvent, due to an additional coordination of methanol leading to six-coordinated vanadium species.

^{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 2-amino-3-methyl-1-pentanol is confirmed by the presence of azomethine proton signals in the spectra of all the complexes. Two-dimensional (COSY, gHSQC and NOESY) NMR experiments were performed for all the compounds which allow to unambiguously establish the attachment of all carbon atoms. For example, the COSY spectrum of the complex **1a** exhibits cross-peaks between the methine proton (major species signal at 3.85 ppm) and one of methylene proton (not separated signal for two protons at 4.80 ppm) and also another methine proton signal (*sec*-butyl substituent) at 2.51 ppm. The bonds between corresponding carbon atoms in the *sec*-butyl side chain are also visible as cross-peaks between the signals of the methyl group protons (1.11 ppm) and the methine proton (2.51 ppm), the methine proton and and both methylene protons (1.13 and 1.49 ppm) and finally cross-peak between methyl group signal at 0.95 ppm and both methylene protons. In case of **1b**, the complex with additional benzohydroxamate co-ligand, the COSY spectrum exhibits separated signals of methylene protons in β-amino alcohol moiety, doublet at 4.70 ppm and doublet of doublets at 4.61 ppm, with cross-peak between latter signal and methine proton signal (doublet of doublets at 4.02 ppm). Moreover, in the NOESY spectra of **1a** and **1b**, cross-peaks between azomethine proton signals and methine proton signals from the ethylene bridge of β-amino alcohol moiety, all of the protons signals of *sec*-butyl moiety and one of the aromatic proton signals are observed. As expected, there is lack of any cross-peaks between the signals of azomethine protons and the methylene protons signals from the above-mentioned ethylene bridge.

3.3. Catalytic activity studies

3.3.1. Sulfoxidation

In this study, the oxidovanadium(V) complexes **1a**–**8a** 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. 5). Aqueous 30% H_2O_2 was 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 3.

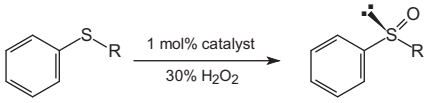

Fig. 5. Sulfoxidation of thioethers catalyzed by vanadium(V) complexes.

Table 3
Catalytic oxidation of PhSMe and PhSBz by aqueous 30% H_2O_2 in presence of 1 mol% vanadium(V) Schiff base complexes as catalysts.

Entry	Catalyst	Substrate	Yield (%)	*T* (°C)	*t* (min)	ee (%)[a]
1	**1a**	PhSMe	85	rt	30	44
2	**2a**	PhSMe	82	rt	30	54
3	**3a**	PhSMe	81	rt	30	56
4	**4a**	PhSMe	83	rt	30	48
5	**5a**	PhSMe	84	rt	30	56
6	**6a**	PhSMe	87	rt	30	52
7	**7a**	PhSMe	84	rt	30	42
8	**8a**	PhSMe	89	rt	30	58
9	**2a**	PhSBz	76	rt	30	29
10	**3a**	PhSBz	74	rt	30	28
11	**5a**	PhSBz	72	rt	30	24
12	**6a**	PhSBz	77	rt	30	26
13	**8a**	PhSBz	73	rt	30	24
14	**2a**	PhSMe	89	−20	180	64
15	**3a**	PhSMe	90	−20	180	68
16	**5a**	PhSMe	85	−20	180	62
17	**6a**	PhSMe	84	−20	180	65
18	**8a**	PhSMe	87	−20	180	67

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

The best results have been obtained for complexes **2a**, **3a**, **5a**, **6a** and **8a** as catalysts in the oxidation of methyl phenyl sulfide (Table 3, entries 2, 3, 5, 6 and 8). An overall yields for all catalysts were in the range of 81–89% within 30 min reaction time and enantiomeric excesses (ee's) of 42–58% for the *R*-configured sulfoxide was obtained. When benzyl phenyl sulfide was used as substrate, possessing more bulky substituent the overall yield of corresponding sulfoxide was distinctly lower (72–77%) and enantioselectivity decreases to value of 24–29% (Table 3, entry 11–15). With the reaction carried out at −20 °C for **2a**, **3a**, **5a**, **6a** and **8a** as catalysts in the oxidation of methyl phenyl sulfide, enantioselectivities improve significantly to 62–68% ee's and a conversion of over 84% of the substrate is observed after 3 h (Table 3, entries 16–20). Mimoun et al. [42] pointed out the importance of sufficiently nucleophilic centre for the oxidative catalysis of organic substances by peroxidovanadium(V) compounds. Better enantioselectivities for **2a**, **3a**, **5a**, **6a** and **8a** 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 centre.

In general, the best results have been obtained in the oxidation reactions of methyl phenyl sulfide with 30% H_2O_2 as oxidant. 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.

3.3.2. Oxidation of styrene

The catalytic potential of the **1a**–**8a** 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. 6). The formation of all these products are presented in Table 4.

In order to achieve suitable reaction conditions for a maximum oxidative conversion of styrene, complex **5a** was taken as a

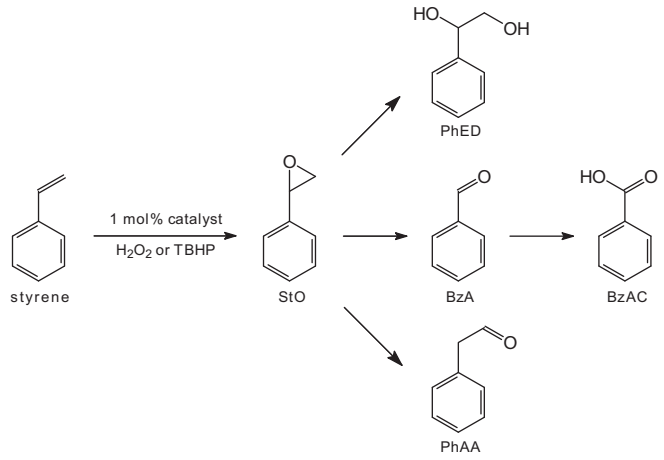

Fig. 6. Various oxidation products of styrene catalyzed by vanadium(V) complexes.

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 M ratios to styrene), different solvents and temperature of the reaction mixture were tested.

To study the effect of amount of 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 CH_3CN (10 ml), and the reaction was carried out for 6 h of contact time at 80 °C. At a H_2O_2 to styrene molar ratio of 1:1, a maximum of 7.3% conversion was achieved. Increasing the ratio to 2:1 improved the conversion to 18.5%, while 3:1 ratio has shown a maximum of 28.6% 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 46.4 to 70.3 and 91.5%, 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 8.7% (H_2O_2) and 45.2% (TBHP) oxidative conversion, while 1 and 2 mol% have shown nearly identical results with 28.6 and 91.5% 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.* 2–5% 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 85% conversion, especially in comparison to the other reported earlier dioxidovanadium(V) complexes with Schiff bases, *i.e.* [VO_2(acac-ambmz)], [VO_2(sal-ambmz)] and [VO_2(sal-aebmz)], which gave 20–35% conversion [43]. Table 4 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 more selective toward benzaldehyde (61.8–67.4%) than styrene oxide (26.7–31.8%). The conversion of the other oxidation products, *i.e.* benzoic acid, phenylacetaldehyde and 1-phenylethane-1,2-diol is very low (>3%). In case of [VO_2(acac-ambmz)], [VO_2(sal-ambmz)] and [VO_2(-sal-aebmz)] complexes, styrene oxide and benzaldehyde were also two main products but with inverted selectivity in comparison to **1a**–**8a**, *i.e.* 50–53% and 37–47%, respectively. Moreover, catalytic activity of oxidovanadium(IV) Schiff base complex derived from *o*-aminobenzyl alcohol, [VO(sal-oaba)], using TBHP as oxidant, has been studied [44], but resulting in very low conversion (16%) and similar selectivity of styrene oxide and benzaldehyde.

When this catalytic reaction have been performed in the same reaction conditions, but with 30% H_2O_2 as oxidant, very low conversion in 6 h of contact time was found (24.2–30.3%). Although the conversion of styrene is distinctly low, the selectivity for benzaldehyde is much better (86.4–88.1%) than in the case of TBHP. On the other hand, as well as for reported earlier [VO_2(acac-ambmz)], [VO_2(sal-ambmz)], [VO_2(sal-aebmz)] [43] and [V^VO(hap-dahp)] complexes [45], styrene oxide is the most expected product but exhibits negligible selectivity (1.2–1.9%). Moreover, the catalytic activity of vanadium(V) complexes encapsulated in the super cages of zeolite-Y, *i.e.* [V^VO(hap-dahp)]-Y [45], [VO_2(sal-ambmz)]-Y, [VO_2(pydx-ambmz)]-Y and [VO_2(pydx-aebmz)]-Y, has recently been discovered [46,47]. The percentage conversion of styrene for [VO_2(pydx-ambmz)]-Y and [VO_2(pydx-aebmz)]-Y is 65–68% and 78% for [V^VO(hap-dahp)]-Y, which is less than that observed

Table 4
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	**1a**	H_2O_2	25.6	1.5	87.6	–	1.2	9.7
2	**2a**	H_2O_2	26.1	1.6	86.8	–	1.4	10.2
3	**3a**	H_2O_2	27.4	1.2	87.0	–	1.3	10.5
4	**4a**	H_2O_2	25.6	1.8	86.1	–	1.2	10.9
5	**5a**	H_2O_2	28.6	1.4	86.7	–	1.7	10.2
6	**6a**	H_2O_2	28.2	1.7	88.1	–	1.1	9.1
7	**7a**	H_2O_2	30.3	1.9	86.4	–	1.1	10.6
8	**8a**	H_2O_2	24.2	1.5	87.0	–	1.3	10.2
9	**1a**	TBHP	88.9	31.7	63.0	1.5	2.4	1.4
10	**2a**	TBHP	87.2	29.2	65.4	1.3	2.6	1.2
11	**3a**	TBHP	90.4	31.8	61.8	1.6	2.9	1.9
12	**4a**	TBHP	89.0	31.3	62.5	1.5	3.0	1.7
13	**5a**	TBHP	91.5	26.7	67.4	1.8	2.5	1.6
14	**6a**	TBHP	88.4	28.4	65.8	1.7	2.8	1.3
15	**7a**	TBHP	86.7	31.2	63.3	1.4	2.3	1.8
16	**8a**	TBHP	87.2	28.0	66.1	1.6	2.8	1.5

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

for VO_2(sal-ambmz)]-Y (97%), but all these catalysts are less selective toward benzaldehyde (*ca.* 55%) and more selective toward 1-phenylethane-1,2-diol (*ca.* 25%). In the presence of H_2O_2, a strong oxidant, 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 [48]. 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 isomerisation of styrene oxide and benzoic acid through oxidation of benzaldehyde, are distinctly much slower processes.

3.3.3. Oxidation of cyclohexene

The oxidation of cyclohexene was achieved with the **1a**–**8a** complexes. In presence of aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as oxidant, the oxidation products obtained are cyclohexene oxide, cyclohexane-1,2-diol, 2-cyclohexene-1-ol and 2-cyclohexene-1-one (Fig. 7). The formation of all these products is presented in Table 5.

As in the case of the oxidation of styrene, complex **5a** was taken as a representative catalyst for optimizing reaction conditions. In this purpose, amount of catalyst (0.5, 1 and 2 mol%) and oxidant (1:1, 2:1 and 3:1 M ratios to cyclohexene), different solvents and temperature of the reaction mixture were also tested.

As acetonitrile and 80 °C were found again an ideal solvent and temperature to run the catalytic reaction, we have studied 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. Cyclohexene (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 H_2O_2 to styrene molar ratio of 1:1, a maximum of 14.6% conversion was achieved. Increasing the ratio to 2:1 improved the conversion to 29.3%, while 3:1 ratio has shown a maximum of 54.7% conversion. Further increment of H_2O_2 shows no improved conversion only marginally, therefore a 3:1 ratio being considered adequate. In case of using TBHP as oxidant, increasing the TBHP:cyclohexene ratio from 1:1 to 2:1 and 3:1 improved the conversion from 41.4 to 67.7 and 88.0%, respectively. As in the previous case, there was no significant conversion improvement upon further addition of oxidant.

Similarly, for three different amounts (*i.e.* 0.5, 1 and 2 mol%) of catalyst and oxidant to cyclohexene molar ratio of 3:1 under above reaction conditions, 0.5 mol% gave only 5.4% (H_2O_2) and 33.6% (TBHP) oxidative conversion, while 1 and 2 mol% of catalyst have shown a maximum conversion with 54.7 for H_2O_2 and 88.0% for TBHP (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.

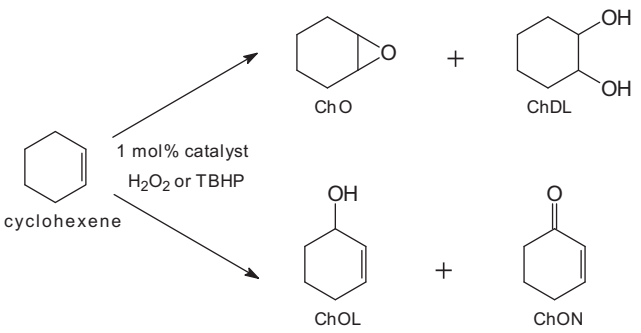

Fig. 7. Various oxidation products of cyclohexene catalyzed by vanadium(V) complexes.

Table 5
Catalytic oxidation of cyclohexene 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 (%)			
				ChO[a]	ChOL[b]	ChON[c]	ChDL[d]
1	**1a**	H_2O_2	57.7	34.8	48.2	3.8	13.2
2	**2a**	H_2O_2	62.6	40.6	42.3	3.0	14.1
3	**3a**	H_2O_2	59.3	37.4	46.6	3.2	12.8
4	**4a**	H_2O_2	56.4	39.6	42.5	3.4	14.5
5	**5a**	H_2O_2	54.7	40.2	44.8	3.7	11.3
6	**6a**	H_2O_2	63.1	43.4	41.7	3.3	11.6
7	**7a**	H_2O_2	53.8	37.2	44.9	2.7	15.2
8	**8a**	H_2O_2	68.4	43.7	37.1	2.9	16.3
9	**1a**	TBHP	75.7	19.0	75.4	4.4	1.2
10	**2a**	TBHP	89.6	16.5	79.0	3.5	1.0
11	**3a**	TBHP	86.2	18.4	76.6	3.9	1.1
12	**4a**	TBHP	81.3	22.4	72.3	4.1	1.2
13	**5a**	TBHP	88.0	16.3	78.2	4.4	1.1
14	**6a**	TBHP	87.2	17.7	76.4	4.9	1.0
15	**7a**	TBHP	80.5	20.6	74.9	3.6	0.9
16	**8a**	TBHP	88.6	18.9	76.0	3.9	1.2

[a] Cyclohexene oxide.
[b] 2-Cyclohexene-1-ol.
[c] 2-Cyclohexene-1-one.
[d] Cyclohexane-1,2-diol.

For **1a**–**8a** as catalysts and with 30% H_2O_2 as oxidant, 53.8–68.4% conversion in 6 h of contact time was found. On the other hand, the conversion of styrene in the same reaction conditions is distinctly lower. The selectivity for cyclohexene oxide (34.8–43.7%) and 2-cyclohexene-1-ol (37.1–48.2%) is much better than for cyclohexane-1,2-diol (11.3–16.3%) and 2-cyclohexene-1-one (2.7–3.8%).

When this catalytic reaction have been performed in the same reaction conditions, but with *tert*-butyl hydroperoxide (TBHP) as oxidant, under the optimized reaction conditions, **1a**–**8a** catalysts gave over 75% conversion. The percentage conversion of styrene and the selectivities for the various reaction products is shown in Table 5. In contrast to H_2O_2 as oxidant, **1a**–**8a** are distinctly more selective toward 2-cyclohexene-1-ol (72.3–79.0%) than cyclohexene oxide (16.3–22.4%) and surprisingly low selectivity of cyclohexane-1,2-diol (*ca.* 1%) and 2-cyclohexene-1-one (3.5–4.9%) is noticed. The reason for the formation of the allylic oxidation products 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 [49].

4. Conclusion

New chiral five-coordinate vanadium(V) complexes derived from Schiff base ligands, monocondensation products of *o*-hydroxycarbonyl compounds with *S*(+)-isoleucinol, and also six-coordinate with the same Schiff bases and bidentate monoanionic benzohydroxamate co-ligand, have been successfully prepared. Those complexes have been characterized by IR, CD, UV–Vis, 1D (^{1}H, ^{51}V) and 2D (COSY, NOESY, gHSQC) NMR and also by X-ray diffraction technique. Moreover, their catalytic properties towards the oxidation of organic sulfides (thioanisole and benzyl phenyl sulfide) and olefins (styrene and cyclohexene) have been studied.

Sulfoxidation reactions have shown that enantioselectivity of vanadium(V) complexes derived from chiral β-amino alcohols is

better and the reaction times are much shorter than for other vanadium(V) complexes with chiral tridentate Schiff bases reported earlier. The results show that the observed yield and enantiomeric excess significantly depend on the nature of the catalyst and substrate 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.

The catalytic potential of the vanadium(V) complexes with tridentate chiral Schiff bases in the oxidation of olefins was also studied, choosing the oxidation of styrene and cyclohexene as the model reactions. These complexes are able to catalyze the oxidative conversion of styrene to styrene oxide and its successive products, and cyclohexene to cyclohexene oxide, cyclohexane-1,2-diol, 2-cyclohexene-1-ol and 2-cyclohexene-1-one by 30% H_2O_2 or *tert*-butyl hydroperoxide as oxidant. It is noticed that catalysts with the electron donating substituents in salicylaldimine moiety gave slightly better conversion. 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 with negligible yield. On the other hand, *tert*-butyl hydroperoxide (TBHP) proved to be an excellent oxidant giving over 85% conversion of styrene with benzaldehyde and styrene oxide as the main products. On the other hand, in the oxidation of cyclohexene much better conversions were found, especially when H_2O_2 was employed as oxidant. But with TBHP as the terminal oxidant similar conversion (up to 90%), in comparison to styrene, and 2-cyclohexene-1-ol with selectivity up to 79% as the main reaction product have been noted.

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