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Oxidovanadium(V) complexes with chiral tridentate Schiff bases derived from *R*(−)-phenylglycinol: Synthesis, spectroscopic characterization and catalytic activity in the oxidation of sulfides and styrene

Grzegorz Romanowski *, Jaromir Kira

Faculty of Chemistry, University of Gdańsk, Sobieskiego 18/19, PL-80952 Gdańsk, Poland

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ABSTRACT

A series of vanadium(V) complexes with chiral tridentate Schiff base ligands, obtained by the single condensation of *R*(−)-phenylglycinol with salicylaldehyde and its derivatives, were prepared. The complexes were characterized by elemental analysis and by their ESI-MS, IR, CD, UV–Vis, 1D (^{1}H, ^{51}V) and 2D (COSY, gHSQC) NMR spectra. The vanadium(V) complexes have the ability to catalyze the oxidation of sulfides [PhSR (R = Me, Bz)] in excellent yields and enantiomeric excesses (over 90%), utilizing aqueous 30% H_2O_2 or cumene hydroperoxide (CHP) as the oxidant. These complexes are also catalytically active in the oxidation of styrene, using aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as the oxidant, to styrene oxide, benzaldehyde, benzoic acid, phenylacetaldehyde and 1-phenylethane-1,2-diol.

1. Introduction

Vanadium is an abundant bioelement in diverse biological systems [1], being found in some classes of enzymes, *e.g.* nitrogenases [2] and haloperoxidases [3]. The discovery of vanadate-dependent haloperoxidases and their importance in various biological catalytic and inhibitory processes has stimulated research on the catalytic aspects of vanadium complexes as model compounds [4,5]. Many such model vanadium(V) Schiff base complexes show catalytic activity towards various organic transformations [6,7]. The salicylaldimine moiety was found to be suitable and found widespread application among the ligands used for complexation to vanadium [8–10]. The main reason for this is that Schiff base ligands and their metal complexes can be easily synthesized and they are efficient catalysts under homogeneous and heterogeneous conditions.

Chiral sulfoxides possess a wide range of biological activities, *e.g.* antimicrobial properties [11], inhibition of the biosynthesis of uric acid [12] and gastric acid secretion [13] or regulation of cholesterol catabolism [14]. Numerous chemical and biological methods for synthesizing chiral sulfoxides have been reported, but metal-catalyzed (including vanadium) enantioselective oxidation of prochiral sulfides is undoubtedly the most direct and economical approach for the synthesis of optically pure sulfoxides. 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 [15,16], the asymmetric alkynylation of aldehydes [16], the epoxidation of cyclooctene [17], the oxidation of bromide [18], the stereoselective synthesis of functionalized tetrahydrofurans [18,19] and oxidative kinetic resolution of α-hydroxy esters [20]. In continuation of our studies on the synthesis, structure, spectroscopic and catalytic properties of vanadium(V) complexes incorporating chiral tridentate Schiff base ligands [21–23], a series of new oxidovanadium(V) complexes comprising coordinated single condensation products of *R*(−)-phenylglycinol with aromatic *o*-hydroxyaldehydes, presented in Fig. 1, have been described. Their spectroscopic properties by 1D and 2D NMR, UV–Vis, CD, IR and ESI-MS have been examined. The catalytic potential of the oxidovanadium(V) complexes in 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 the oxidant has been studied. Moreover, these complexes were also used as catalysts in the oxidation of styrene, using aqueous 30% H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as the oxidant.

* Tel.: +48 585235341.
E-mail address: greg@chem.univ.gda.pl (G. Romanowski).

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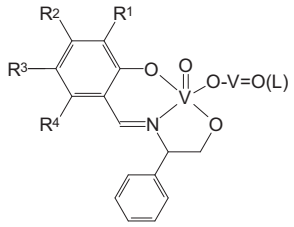

	R^1	R^2	R^3	R^4
1	H	H	H	H
2	OCH_3	H	H	H
3	H	H	OCH_3	H
4	H	OCH_3	H	OCH_3
5	H	H	CH_3	H
6	H	H	Br	H
7	H	H	NO_2	H
8	H	OH	H	H
9	$C(CH_3)_3$	H	H	H
10	H	H	$-(CH)_4-$	

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

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 a Perkin-Elmer LAMBDA 18 spectrophotometer. Circular dichroism spectra were measured with a Jasco J-815 spectropolarimeter. ESI–MS measurements were performed in MeOH solutions with a Bruker Daltonics HCTultra mass spectrometer (ion trap). 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 a catalyst (0.010 mmol) in 3 ml of CH_2Cl_2/MeOH solution (7:3, v/v), a sulfide (1.00 mmol) was added at room temperature or −20 °C, together with 1,3,5-trimethoxybenzene as an internal standard. Aqueous 30% H_2O_2 or cumene hydroperoxide (CHP) as the oxidant was added (1.10 mmol) in 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 ^1H NMR spectra in the presence of the chiral shift reagent Eu(hfc)$_3$ (where Hhfc is 3-(heptafluoropropylhydroxymethylene)-(+)-camphoric acid) [24].

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 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 the GC yield based on the starting styrene. The identity of the oxidation products were confirmed by GC–MS. The influence of the amounts of catalyst and oxidant were also studied to check their effect on the conversion and selectivity of the reaction products.

2.3. Complexes

The complexes were obtained by the following example procedure. A solution of 5 mmol of *R*(−)-phenylglycinol 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 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-[(1-oxido-2-phenylethyl)iminomethyl]phenolato-κ^3N,O,O′}oxidovanadium(V)) (**1**)

Yield 83%. *Anal.* Calc. for $C_{30}H_{26}N_2O_7V_2$: C, 57.3; H, 4.2; N, 4.5. Found: C, 57.4; H, 4.3; N, 4.5%. IR (KBr, cm^{-1}): 1621 ($\nu_{C=N}$); 978 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 280 (8860), 343 (3710). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 279 (−1.84), 312 (4.02), 363 (−5.32). ^1H NMR (CD_3OD, ppm) major (60%): 8.27 (1H, s) (azomethine); 7.51 (3H, s), 7.43 (3H, m), 7.36 (2H, m), 6.84 (1H, d, ^4J = 3 Hz) (aromatic); 5.13 (1H, t, ^3J = 8 Hz), 4.81 (1H, ov) (methylene); 5.00 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz) (methine); minor (40%): 8.39 (1H, s) (azomethine); 7.49 (3H, s), 7.45 (3H, ov), 7.39 (2H, ov), 6.94 (1H, d, ^4J = 3 Hz) (aromatic); 5.65 (1H, t, ^3J = 8 Hz), 5.15 (1H, ov), (methylene); 4.98 (1H, ov) (methine). ^{51}V NMR (CD_3OD, ppm) major (60%): −532.1, minor (40%): −535.9. ESI–MS (*m/z*): 696.7 [$V_2O_3L_2$–H^+ + CH_3OH + $2H_2O$].

2.3.2. μ-Oxido-bis({R(−)-2-[(1-oxido-2-phenylethyl)iminomethyl]-6-methoxyphenolato-κ^3N,O,O′}oxidovanadium(V)) (**2**)

Yield 85%. *Anal.* Calc. for $C_{32}H_{30}N_2O_9V_2$: C, 55.8; H, 4.4; N, 4.1. Found: C, 55.7; H, 4.5; N, 4.0%. IR (KBr, cm^{-1}): 1628 ($\nu_{C=N}$); 984 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 281 (8740), 346 (3680). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 283 (−2.18), 314 (2.84), 372 (−4.15). ^1H NMR (CD_3OD, ppm) major (60%): 8.24 (1H, s) (azomethine); 7.38–7.50 (5H, m), 7.14 (1H, d, ^3J = 8 Hz), 6.89 (1H, d, ^3J = 8 Hz), 6.78 (1H, t, ^3J = 8 Hz) (aromatic); 5.16 (1H, t, ^3J = 8 Hz), 4.82 (1H, ov) (methylene); 5.02 (1H, dd, ^3J = 8 Hz, ^4J = 3 Hz) (methine); 3.87 (3H, s) (methoxy); minor (40%): 8.39 (1H, s) (azomethine); 7.32–7.42 (5H, m), 7.18 (1H, d, ^3J = 8 Hz), 6.99 (1H, d, ^3J = 8 Hz), 6.84 (1H, t, ^3J = 8 Hz) (aromatic); 5.67 (1H, t, ^3J = 8 Hz), 5.18 (1H, ov) (methylene); 5.00 (1H, ov) (methine); 3.89 (3H, s) (methoxy). ^{51}V NMR (CD_3OD, ppm) major (60%): −528.8; minor (40%): −531.7. ESI–MS (*m/z*): 756.8 [$V_2O_3L_2$–H^+ + CH_3OH + $2H_2O$].

2.3.3. μ-Oxido-bis({R(−)-2-[(1-oxido-2-phenylethyl)iminomethyl]-4-methoxyphenolato-κ^3N,O,O′}oxidovanadium(V)) (**3**)

Yield 87%. *Anal.* Calc. for $C_{32}H_{30}N_2O_9V_2$: C, 55.8; H, 4.4; N, 4.1. Found: C, 55.8; H, 4.5; N, 4.1%. IR (KBr, cm^{-1}): 1625 ($\nu_{C=N}$); 982 ($\nu_{V=O}$). UV–Vis spectrum in MeOH [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 284 (9030), 353 (3860). CD spectrum in MeOH [λ_{max} (nm), $\Delta\varepsilon$ (M^{-1} cm^{-1})]: 281 (−2.07), 313 (2.56), 369 (−5.13). ^1H NMR (CD_3OD, ppm) major (60%): 8.27 (1H, s) (azomethine); 7.38–7.50 (5H, m),