Bis[2-(oxazolinyl)phenolato]oxovanadium(IV) Complexes: Syntheses, Crystal Structures and Catalyses

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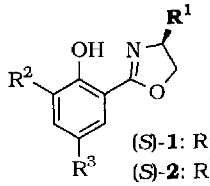
The syntheses and X-ray crystal structures of two chiral bis[2-(oxazolinyl)phenolato]-oxovanadium(IV) complexes are reported. Their catalytic activity in oxidative transformations and C–C bond-forming reactions has been investigated.

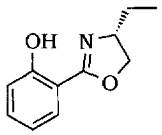
(Hydroxyphenyl)oxazolines serve as chelating units in microbial metal-transporting agents, which show high affinity and specificity for iron(III)[1]. Various derivatives can readily be synthesized by a metal-catalyzed condensation reaction of hydroxybenzonitriles and 2-amino alcohols[2]. Several metal complexes bearing 2-(oxazolinyl)phenolato ligands have been synthesized[3–7] and their solid-state structures were determined[5–7]. Of particular interest are chiral bis[2-(oxazolinyl)phenolato]copper(II) complexes, which catalyze asymmetric Baeyer-Villiger oxidations[8,9]. Other metal complexes of this type have been used in cyclopropanations[10], allylic functionalizations[3] and Lewis-acid-catalyzed C–C bond-forming reactions[11]. In stereoselective polymerization reactions, cationic d^0 complexes are believed to be the key species[7,12]. Our recent interest in the use of vanadium catalysts in asymmetric oxidations[13,14] turned our attention towards bis[2-(oxazolinyl)phenolato]oxovanadium(IV) complexes[15]. Their preparations are described herein. The molecular structures of two complexes of this type were determined by X-ray crystallography. The catalytic properties of these complexes in oxidative transformations and C–C bond-forming reactions have been investigated.

Syntheses and Crystal Structures of (*S,S*)-5 and (*R,R*)-6

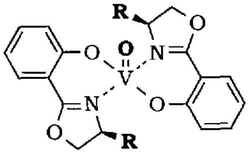
2-(Hydroxyphenyl)oxazolines (*S*)-**1**–**3** and (*R*)-**4** were synthesized according to our published procedure[2]. Refluxing of the colorless solutions of (*S*)-**1** and (*R*)-**4** in toluene with 0.5 equivalents of vanadyl acetylacetonate [VO(acac)$_2$], followed by evaporation of the solvent gave (*S,S*)-**5** and (*R,R*)-**6**, respectively, as violet solids. Recrystallization from ethanol afforded violet needles [(*S,S*)-**5**] and plates [(*R,R*)-**6**]. 2-(Hydroxyphenyl)oxazolines (*S*)-**2** and (*S*)-**3**, having sterically more demanding substituents at the aryl and oxazoline units, did not give the corresponding vanadium complexes even after prolonged reaction times.



(*S*)-**1**: R^1 = *i*Pr, R^2 = R^3 = H
(*S*)-**2**: R^1 = R^2 = *t*Bu, R^3 = H
(*S*)-**3**: R^1 = R^2 = *t*Bu, R^3 = NO_2



(*R*)-**4**



(*S,S*)-**5**: R = *i*Pr
(*S,S*)-**6**: R = Et

The molecular structures of vanadium complexes (*S,S*)-**5** and (*R,R*)-**6** were unambiguously established by X-ray crystal structure determinations. These studies also confirmed the absolute configurations. Full ORTEP plots are given in Figures 1 and 2[16].

In the complexes (*S,S*)-**5** and (*R,R*)-**6**, two homochiral dianionic ligands are bound to the metal giving a square-pyramidal coordination geometry around vanadium. The oxazoline N and phenolato O atoms in each complex are located in an almost square-planar arrangement. The oxygens of the vanadyl moieties are positioned above these planes. The values of the bond angles for N(1)-V(1)-N(1′) are 155.8(2)° [(*S,S*)-**5**] and 153.3(2)° [(*R,R*)-**6**]. Interestingly, in both complexes the vanadyl oxygens are on the same side as the oxazoline substituents (isopropyl or ethyl). The bulky methyl groups at the termini of these substituents point to the outer sphere of the complexes. The vanadyl V-O bond

0009–2940/97/0707–0887 $ 17.50+.50/0

Figure 1. Molecular structure of (*S,S*)-**5**

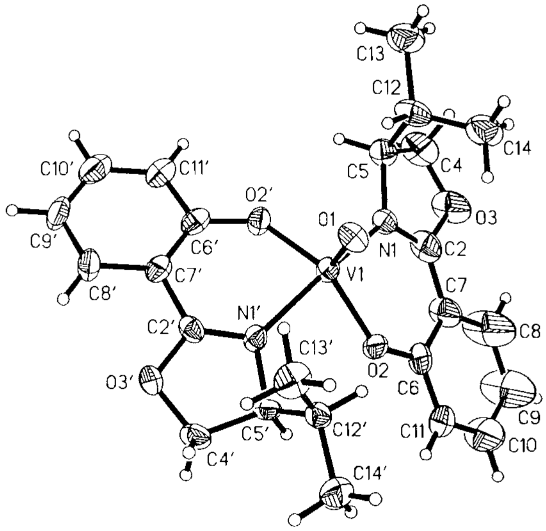
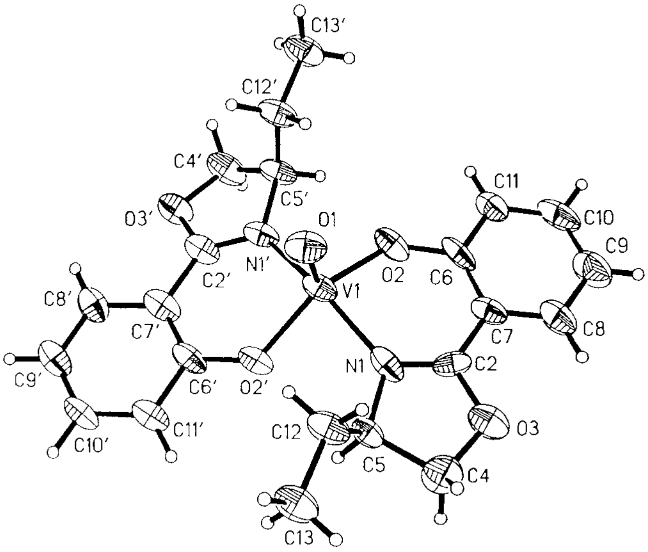


Figure 2. Molecular structure of (*R,R*)-**6**



lengths in (*S,S*)-**5** [1.602(4) Å] and (*R,R*)-**6** [1.605(5) Å] are almost identical.

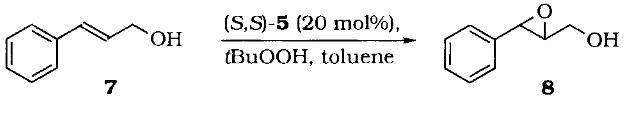
Catalytic Properties of (*S,S*)-5 and (*R,R*)-6

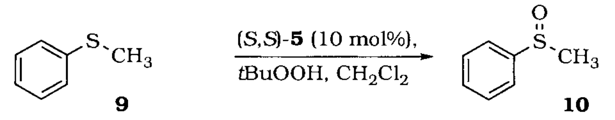
Various oxidative transformations are known to be catalyzed by oxovanadium complexes[13,14,17]. With this in mind, we first investigated the epoxidation of cinnamyl alcohol (**7**) with *tert*-butyl hydroperoxide[18–20]. In the presence of 20 mol% of (*S,S*)-**5**, epoxy alcohol **8** was obtained in 40% yield. HPLC analysis using a chiral column showed the product to be a racemic mixture.

Next, we focussed on vanadium-catalyzed sulfide oxidations[13,14,20]. Use of 10 mol% of (*S,S*)-**5** in the oxidation of methyl phenyl sulfide (**9**) with *tert*-butyl hydroperoxide in dichloromethane gave the corresponding sulfoxide **10** in 70% yield. Again, a racemic product was obtained.

Table 1. Selected bond lengths (Å), angles (°) and torsion angles (°) for (*S,S*)-**5** and (*R,R*)-**6**

Distances/Angles:	(*S,S*)-5	(*R,R*)-6
V(1)-O(1)	1.602(4)	1.605(5)
V(1)-N(1)	2.075(5)	2.050(7)
V(1)-N(1')	2.068(5)	2.087(7)
V(1)-O(2)	1.915(4)	1.920(5)
V(1)-O(2')	1.916(4)	1.924(4)
N(1)-V(1)-O(1)	101.7(2)	103.9(3)
N(1)-V(1)-N(1')	155.8(2)	153.3(2)
O(2)-V(1)-O(1)	112.3(2)	110.9(3)
O(2)-V(1)-O(2')	135.3(2)	139.8(2)
N(1)-V(1)-O(2)	85.2(2)	86.4(2)
N(1)-V(1)-O(2')	85.4(2)	85.3(2)
N(1)-V(1)-O(2)-C(6)	-1.6(6)	-14.9(7)
N(1)-C(2)-C(7)-C(6)	0(2)	-3.4(13)
N(1)-V(1)-N(1')-C(5')	96.5(6)	-100.4(7)
N(1)-V(1)-N(1')-C(5')	69.7(7)	-55.6(8)





Attempts to use vanadium complex (*S,S*)-**5** as an activating Lewis acid in carbonyl addition reactions did not meet with any success. No product was formed by mixing dichloromethane solutions of trimethylsilyl cyanide or allyltributyltin with benzaldehyde in the presence of 10 mol% and 20 mol% of (*S,S*)-**5**, respectively[21,22]. Togni has demonstrated that oxovanadium(IV) complexes bearing camphor-derived 1,3-diketonato ligands catalyze asymmetric hetero Diels-Alder reactions[23]. However, in the presence of 5 mol% of (*S,S*)-**5** no cycloaddition between 1-methoxy-3-[(trimethylsilyl)oxy]butadiene and benzaldehyde took place.

Conclusion

We have synthesized structurally well-defined chiral bis[2-(oxazolinyl)phenolato]oxovanadium complexes and have demonstrated their potential in catalytic oxidative transformations such as epoxidations and sulfide oxidations. With (*S,S*)-**5** and (*R,R*)-**6** only racemic products were obtained. The Lewis-acidity of these complexes is insufficient to activate carbonyl compounds for addition reactions. We are currently searching for other applications of these new catalysts in synthesis.

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Experimental Section

All reactions were carried out in flame-dried glassware under argon using anhydrous solvents. Solvents were evaporated under reduced pressure using a Büchi rotary evaporator. All solvents were purified prior to use. – MS: Varian CH 7 A. – IR: Bruker IFS 88. – Elemental analyses were performed with a Heraeus CHN-Rapid. 2-(Hydroxyphenyl)oxazolines (*S*)-**1**–**3** and (*R*)-**4** were synthesized according to the published procedure[2].

General Procedure of the Syntheses of (S,S)-**5** *and (R,R)*-**6**: A mixture of VO(acac)$_2$ (0.53 g, 2 mmol) and the ligand (4 mmol) in toluene (20 ml) was refluxed for 24 h. After cooling the solution to room temperature, the solvent was removed *in vacuo* (at 120°C). The remaining solid was recrystallized from ethanol.

(*S,S*)-**5**: 0.661 g (70%), violet needles; m.p. >250°C (ethanol). – IR (KBr): $\tilde{\nu}$ = 3433, 2962, 1616, 1591, 1485, 1477, 1399, 1387, 1332, 1264, 1240, 1079, 978, 954, 863 cm^{-1}. – MS (EI, 70 eV); *m/z* (%): 476 (28), 475 (100) [M$^+$], 457 (16), 389 (16), 303 (16), 227 (28), 185 (29), 67 (4). – $C_{24}H_{28}N_2O_5V$ (475.44): calcd. C 60.57, H 5.93, N 5.89; found C 60.40, H 5.99, N 5.73.

(*R,R*)-**6**: 0.672 g (75%), violet plates; m.p. 185–188°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3436, 2962, 1616, 1589, 1479, 1444, 1395, 1330, 1247, 1233, 991, 859, 671 cm^{-1}. – MS (EI, 70 eV); *m/z* (%): 448 (36), 447 (100) [M$^+$], 429 (10), 375 (15), 303 (15), 257 (11), 185 (38), 67 (4). – $C_{22}H_{24}N_2O_5V$ (447.38): calcd. C 59.06, H 5.41, N 6.26; found C 59.09, H 5.33, N 6.19.

Crystal Structure Analyses of (S,S)-**5** *and (R,R)*-**6**: Unit cell parameters were determined by centering 20 [(*S,S*)-**5**] and 18 [(*R,R*)-**6**] strong, independent reflections. Data collections were performed on a Siemens *P*4 four-circle diffractometer. The usual corrections were applied. The structures were solved by direct methods using the program XS in SHELXTL-Plus (Sheldrick, 1990). Anisotropic least-squares refinement was carried out on all non-H atoms using the program SHELXL-93 (Sheldrick, 1993). Hydrogen atoms are in calculated positions. Scattering factors were taken from the International Tables for Crystallography, Vol. IV, Table 2.2B. Crystal data and other numerical details of the structure determination are listed in Table 2.

Catalyzed Epoxidation: To a solution of 67.09 mg (0.5 mmol) of cinnamyl alcohol (**7**) and (*S,S*)-**5** (47.5 mg, 0.1 mmol) in dry toluene (2 ml) at 0°C, was added dropwise *tert*-butyl hydroperoxide (80% in di-*tert*-butyl peroxide, 0.1 ml, 1 mmol). The mixture was slowly warmed to ambient temperature and stirred for 16 h. Diethyl ether (100 ml) was added and the resulting solution was extracted with saturated aqueous NaHCO$_3$ solution (3 × 50 ml). The organic phase was separated, washed with brine, and dried over Na$_2$SO$_4$. The solvent was evaporated *in vacuo* and the product was purified by flash chromatography to afford 30 mg of epoxide **8** (40%).

Catalyzed Sulfide Oxidation: In a test tube at 0°C, a solution of 47.5 mg (0.1 mmol) of (*S,S*)-**5** and 124 mg (1 mmol) of methyl phenyl sulfide (**9**) in 2 ml of dichloromethane was treated dropwise with 0.16 ml (1.6 mmol) of *tert*-butyl hydroperoxide (80% in di-*tert*-butyl peroxide). After stirring at room temperature for 18 h, the solvent was removed *in vacuo* and the product was isolated by column chromatography (SiO$_2$, *tert*-butyl methyl ether) to give 98 mg (70%) of sulfoxide **10**.

Table 2. Crystal data and details of refinements

	(*S,S*)-**5**	(*R,R*)-**6**
chemical formula	$C_{24}H_{28}N_2O_5V$	$C_{22}H_{24}N_2O_5V$
crystal size	0.35 x 0.3 x 0.25	0.4 x 0.3 x 0.2
crystal system	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
Z	4	4
a [pm]	1009.0(1)	834.4(1)
b [pm]	1177.9(3)	1126.3(4)
c [pm]	1982.5(3)	2213.4(3)
volume [x 10^{-30} m^3]	2356.2(7)	2080.1(8)
F(000)	996	932
ρcalcd [Mg•m^{-3}]	1.340	1.429
θmax °	22.51	22.01
radiation (wavelength [pm])	MoK_α (71.073)	MoK_α (71.073)
scan mode	ω	ω
temperature of measurement [K]	173(2)	173(2)
no. of measured reflections	4299	3741
no. of independent reflections	3065	2551
no. of reflections included in refinement	3060	2551
Flack-parameter	-0.02(5)	-0.07(7)
μ [mm^{-1}]	0.458	0.513
no. of parameters	294	274
R (on *F*, for 2590 and 2130 refl.) [a] [I>2σ(I)]	0.0484	0.0678
wR2 (on F^2, all data) [b]	0.1505	0.1985
weight param. p,q	0, 6.6297	0.1426, 0
GOF (on F^2)	1.135	1.117
ρ [x 10^{30}e•m^{-3}]	0.424/-0.755	0.704/-1.468

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. – [b] $wR2 = \sqrt{[w(F_o^2 - F_c^2)^2/\Sigma(F_o)^2]}$, $w = 1/\sigma^2(F_o^2) + (pP)^2 + qP$, $P = (F_o^2 + 2F_c^2)/3$.

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[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (deposition number 100091). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code +(1223) 336–033, e-mail: teched@chemcrys.cam.ac.uk).

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