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Preparation and Characterization of Optically Active Schiff Base-Oxovanadium(IV) and -Oxovanadium(V) Complexes and Catalytic Properties of These Complexes on Asymmetric Oxidation of Sulfides into Sulfoxides with Organic Hydroperoxides

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Oxovanadium(V) complexes, $\mathrm{V^{V}O}$ (Schiff base)Y (Y=$\mathrm{ClO_4}$, Cl, $\mathrm{NO_3}$), with quadridentate Schiff base ligands derived from optically active 1,2-diamines and salicylaldehyde or its derivatives were prepared by oxidizing the corresponding $\mathrm{V^{IV}O}$ (Schiff base) with $\mathrm{Ce^{IV}}$ in acetonitrile followed by the addition of HY. The complexes were characterized by their ^{1}H NMR, IR, UV-Vis, and circular dichroism spectra, and electrochemistry. Reversible reduction potentials ($\mathrm{V^{5+}/V^{4+}}$) obtained by cyclic voltammetry for a series of oxovanadium(V) complexes with Schiff base ligands derived from 5-substituted salicylaldehydes showed a linear dependence on the Hammett parameter. Both the vanadium(IV) and the vanadium(V) complexes catalyze asymmetric oxidation of sulfides into the corresponding sulfoxides with organic hydroperoxides. The oxovanadium(IV) complex catalysts gave much better asymmetric induction than the oxovanadium(V) complex catalysts and in most cases the enantiomeric excess (ee) ranged between 20 and 40%. In the reaction of $\mathrm{V^{IV}O}$ (Schiff base) with an organic hydroperoxide the complex is finally converted into the oxovanadium(V) species, and a dark brown intermediate is suggested to be the catalytically active species.

In recent years, much attention is being attracted to the usefulness of optically active sulfoxides in the asymmetric synthesis of organic compounds.[1] An efficient asymmetric oxidation of prochiral organic sulfides into optically active sulfoxides has been reported, using a modified Sharpless reagent (Ti(OPr^i)$_4$/diethyl (*R*,*R*)-tartrate/Bu^{t}OOH) for asymmetric epoxidation.[2,3]

In a previous paper,[4] we reported that optically active Schiff base-oxovanadium(IV) complexes catalyze the asymmetric oxidation of sulfides into the corresponding sulfoxides with organic hydroperoxides. Recently, we found that in the reaction of Schiff base-oxovanadium(IV) complexes with an organic hydroperoxide the complex is finally converted into the oxovanadium(V) species. Curci et al.[5] studied the kinetics of the oxidation of dibutyl sulfide with *t*-butyl hydroperoxide catalyzed by VO(acac)$_2$ (acac=2,4-pentanedionate ion), and found that the catalytically active species is a vanadium(V) and not a vanadium(IV) species. These results led us to study the catalytic properties of the Schiff base-oxovanadium(V) complexes.

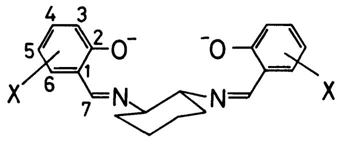
This paper reports the preparation and properties of a series of oxovanadium(IV) and oxovanadium(V) complexes with quadridentate Schiff base ligands derived from optically active 1,2-diamines and salicylaldehyde or its derivatives, and the asymmetric oxidation of sulfides into sulfoxides with organic hydroperoxides catalyzed by these complexes.

Experimental

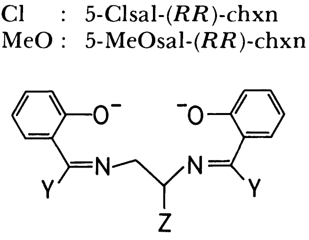
(*R*)-1,2-Propanediamine ((*R*)-pn) and (*R*,*R*)-1,2-cyclohexanediamine ((*RR*)-chxn) were obtained by the published methods.[6,7]

(*R*)-pn: $[\alpha]_D$ −11.0° (*c* 1.6, H$_2$O); lit, $[\alpha]_D$ −11.0° (*c* 2.5, H$_2$O).[6]

(*RR*)-chxn: $[\alpha]_D$ −44.1° (*c* 2.4, MeOH); lit, $[\alpha]_D$ −44.1° (*c* 3.0, MeOH).[7]



X=H : sal-(*RR*)-chxn
3-MeO : 3-MeOsal-(*RR*)-chxn
3-EtO : 3-EtOsal-(*RR*)-chxn
3-Bu^t : 3-Bu^{t}sal-(*RR*)-chxn
4-MeO : 4-MeOsal-(*RR*)-chxn
5-NO$_2$: 5-NO$_2$sal-(*RR*)-chxn
5-Br : 5-Brsal-(*RR*)-chxn
5-Cl : 5-Clsal-(*RR*)-chxn
5-MeO : 5-MeOsal-(*RR*)-chxn



Y=Z=H : salen
Y=H, Z=CH$_3$: sal-(*R*)-pn
Y=Z=CH$_3$: 7-Mesal-(*R*)-pn

Scheme 1.

Table 1. Analytical Data and Colors of the Complexes

Complex	Formula	Found (Calcd)			Color
		C/%	H/%	N/%	
Vanadium(IV) complexes					
VO(3-MeOsal-(*RR*)-chxn)	$C_{22}H_{24}N_2O_5V$	58.44(59.06)	5.50(5.41)	6.14(6.26)	Green
VO(3-EtOsal-(*RR*)-chxn)	$C_{24}H_{28}N_2O_5V$	60.34(60.63)	5.91(5.94)	6.01(5.89)	Green
VO(3-Bu^{t}sal-(*RR*)-chxn)	$C_{28}H_{36}N_2O_3V$	66.71(67.32)	7.01(7.26)	5.69(5.61)	Green
VO(4-MeOsal-(*RR*)-chxn)	$C_{22}H_{24}N_2O_5V$	59.00(59.06)	5.48(5.41)	6.22(6.26)	Green
VO(5-NO_2sal-(*RR*)-chxn)·0.5H_2O	$C_{20}H_{19}N_4O_{7.5}V$	49.56(49.39)	3.83(3.94)	11.48(11.52)	Orange
VO(5-Brsal-(*RR*)-chxn)	$C_{20}H_{18}N_2Br_2O_3V$	44.29(44.07)	3.32(3.33)	5.01(5.14)	Green
VO(5-Clsal-(*RR*)-chxn)	$C_{20}H_{18}N_2Cl_2O_3V$	52.61(52.65)	3.84(3.98)	6.08(6.14)	Green
VO(5-MeOsal-(*RR*)-chxn)	$C_{22}H_{24}N_2O_5V$	58.98(59.06)	5.39(5.41)	6.17(6.26)	Green
Vanadium(V) complexes					
VO(salen)ClO_4	$C_{16}H_{14}N_2ClO_7V$	44.07(44.42)	3.25(3.26)	6.29(6.47)	Dark green
VO(sal-(*RR*)-chxn)ClO_4	$C_{20}H_{22}N_2ClO_8V$	47.48(47.59)	4.28(4.39)	5.76(5.55)	Dark violet
VO(sal-(*RR*)-chxn)Cl·3H_2O	$C_{20}H_{26}N_2ClO_6V$	50.69(50.38)	5.31(5.50)	5.90(5.87)	Dark green
VO(sal-(*RR*)-chxn)NO_3·0.5H_2O	$C_{20}H_{21}N_3O_{6.5}V$	52.49(52.41)	4.63(4.62)	8.98(9.17)	Dark green
VO(3-MeOsal-(*RR*)-chxn)ClO_4·0.5H_2O	$C_{22}H_{25}N_2ClO_{9.5}V$	47.43(47.54)	4.32(4.53)	5.10(5.04)	Dark brown
VO(3-MeOsal-(*RR*)-chxn)Cl·3H_2O	$C_{22}H_{30}N_2ClO_8V$	48.89(49.21)	5.47(5.63)	5.40(5.22)	Dark brown
VO(5-NO_2sal-(*RR*)-chxn)ClO_4	$C_{20}H_{18}N_4ClO_{11}V$	42.29(42.04)	3.30(3.35)	10.57(10.64)	Dark violet
VO(5-Brsal-(*RR*)-chxn)ClO_4·H_2O	$C_{20}H_{20}N_2Br_2ClO_8V$	36.09(36.26)	2.92(3.04)	4.28(4.23)	Dark green
VO(5-Clsal-(*RR*)-chxn)ClO_4·H_2O·0.5CH_3CN	$C_{21}H_{21.5}N_{2.5}Cl_3O_8V$	42.63(42.45)	3.55(3.65)	6.22(5.89)	Dark green
VO(5-MeOsal-(*RR*)-chxn)ClO_4·H_2O	$C_{22}H_{26}N_2ClO_{10}V$	47.08(46.78)	4.47(4.64)	5.24(4.96)	Dark green
VO(5-MeOsal-(*RR*)-chxn)Cl·2H_2O	$C_{22}H_{28}N_2ClO_7V$	50.79(50.93)	5.22(5.44)	5.34(5.40)	Dark green
VO(sal-(*R*)-pn)ClO_4·0.5H_2O	$C_{17}H_{17}N_2ClO_{7.5}V$	44.58(44.81)	3.59(3.76)	5.96(6.15)	Dark green
VO(7-Mesal-(*R*)-pn)ClO_4·2.5H_2O	$C_{19}H_{25}N_2ClO_{9.5}V$	43.41(43.90)	5.02(4.85)	5.46(5.39)	Dark green

Schiff bases were prepared in situ (EtOH) or using the methods of Gullotti et al.[8] VO(sal-(*RR*)-chxn), VO(sal-(*R*)-pn), and VO(7-Mesal-(*R*)-pn) were prepared by the method of Farmer and Urbach.[9]

$\mathrm{V^{IV}O}$(Schiff base) (Schiff base=3-MeOsal-(*RR*)-chxn, 3-EtOsal-(*RR*)-chxn, 3-Bu^{t}sal-(*RR*)-chxn, 4-MeOsal-(*RR*)-chxn, 5-NO_2sal-(*RR*)-chxn, 5-Brsal-(*RR*)-chxn, 5-Clsal-(*RR*)-chxn, 5-MeOsal-(*RR*)-chxn). The procedure is described for VO(3-MeOsal-(*RR*)-chxn). The other complexes were prepared by similar procedures. To an ethanol solution (60 cm^3) containing (*RR*)-chxn (2.28 g, 2.0×10^{-2} mol) and 3-methoxysalicylaldehyde (6.08 g, 4.0×10^{-2} mol) was added an aqueous solution (60 cm^3) of $VOSO_4\cdot4H_2O$ (4.5 g, 2.1×10^{-2} mol) with stirring. The mixture was refluxed for 10 min and cooled to room temperature to give green crystals, which were filtered, and washed with water and acetone. Recrystallization was carried out from dichloromethane by the addition of acetone. Yield: 4.0 g (43%).

The analytical data and colors of the complexes are given in Table 1.

$\mathrm{V^{V}O}$(Schiff base)Y (Schiff base=salen, sal-(*RR*)-chxn, 3-MeOsal-(*RR*)-chxn, 5-NO_2sal-(*RR*)-chxn, 5-Brsal-(*RR*)-chxn, 5-Clsal-(*RR*)-chxn, 5-MeOsal-(*RR*)-chxn, sal-(*R*)-pn, 7-Mesal-(*R*)-pn; Y=ClO_4, Cl, NO_3). These complexes were prepared by a similar method, and a representative procedure is given for VO(sal-(*RR*)-chxn)ClO_4. To a suspension of $\mathrm{V^{IV}O}$(sal-(*RR*)-chxn) (0.387 g, 1.0×10^{-3} mol) in acetonitrile (50 cm^3) was added an acetonitrile solution (60 cm^3) of $(NH_4)_2Ce(NO_3)_6$ (0.658 g, 1.2×10^{-3} mol) with stirring. The resulting deep violet solution was evaporated to ca. 30 cm^3 under reduced pressure. The mixture was filtered, and to the filtrate 1.5 M $HClO_4$ (30 cm^3, 1 M=1 mol dm^{-3}) was added to give dark violet crystals. They were collected by filtration, and recrystallized from acetonitrile by the addition of 1.5 M $HClO_4$. Yield: 0.45 g (89%).

The corresponding chloro and nitrato complexes were prepared by a method similar to that for the perchlorato complex, 1.5 M HCl and 1.5 M HNO_3, respectively, being used instead of 1.5 M $HClO_4$.

The $\mathrm{V^{V}O}$(Schiff base)Y complexes can be prepared by oxidizing $\mathrm{V^{IV}O}$(Schiff base) with 1-methyl-1-phenylethyl hydroperoxide. To a dichloromethane solution (100 cm^3) of VO(salen) (1.5×10^{-3} mol) was added 1-methyl-1-phenylethyl hydroperoxide (1.5×10^{-2} mol), and the solution was left at room temperature overnight. The solvent was removed under reduced pressure, and the residue was dissolved in acetonitrile (20 cm^3). The solution was mixed with 2 M HCl (40 cm^3) to yield green crystals. Yield: 68%. The ^{1}H NMR spectrum in DMSO-*d*$_6$ (dimethyl-*d*$_6$ sulfoxide) was identical with that of VO(salen)Cl prepared by the above method.

The analytical data and colors of the complexes prepared by the former method are given in Table 1.

Oxidation of Sulfides by Organic Hydroperoxides with a Catalytic Amount of Schiff Base-Oxovanadium(IV) or -Oxovanadium(V) Complexes. A typical run is given for the oxidation of methyl phenyl sulfide with 1-methyl-1-phenylethyl hydroperoxide catalyzed by $\mathrm{V^{IV}O}$(3-MeOsal-(*RR*)-chxn). VO(3-MeOsal-(*RR*)-chxn) (4.0×10^{-5} mol) was reacted with a dichloromethane solution (8 cm^3) of 1-methyl-1-phenylethyl hydroperoxide (5.0×10^{-4}mol) in a 10 cm^3 volumetric flask for 4—5 h at 25 °C. The resulting dark brown solution was cooled to 0 °C. Methyl phenyl sulfide (4.0×10^{-4} mol) was added, and the solution was diluted to the mark (10 cm^3) with dichloromethane. The mixture was kept at 0 °C for 14 h. The solvent was removed under reduced pressure, and the residue was extracted with diethyl ether, which was evaporated under reduced pressure. From the resulting oil, methyl phenyl sulfoxide was isolated and purified by column chromatography on silica gel (eluent: cyclohexane–ethyl acetate (1:1 v/v)). Yield: 81%. The enantiomeric excess (ee) was determined on the basis of the reported optical rotation of the pure enantiomer;[10] $[\alpha]_D$ −60.8° (*c* 0.80, acetone); ee 41% (*S*). The ee could also be determined from the circular dichroism (CD) spectrum on the basis of $\Delta\varepsilon_{237}=-13.9$ for the pure (*S*)-isomer in acetonitrile–water (6:4 v/v).

The kinetics of these oxidation reactions was studied by high-performance liquid chromatography. Portions of the reaction mixture were withdrawn at intervals and then chromatographed (sample volume, 4×10^{-3} cm^3) with a column (ϕ 0.46 cm×25 cm) of Develosil ODS-5 (Nomura Chemical Co., Ltd.) and acetonitrile–water (6:4 v/v) as an eluent. Chromatography was carried out with a JASCO Tri Rotar V system at a flow rate of 1.5 cm^3 min^{-1} and the components were detected with a JASCO UVIDEC 100 IV spectrophotometric detector at 260 nm. The amounts of sulfide, sulfoxide, and sulfone were determined from the absorption spectra of the collected fractions or by paper cutouts matching the bands in the elution curve, taking the molar absorption coefficients into consideration.

Measurements. IR, UV-Vis, and CD spectra were recorded on a JASCO A-3 spectrophotometer, a Hitachi U-3400 spectrophotometer, and a JASCO J-40CS spectropolarimeter, respectively. ^{1}H NMR spectra were recorded on a JEOL GX-400 spectrometer using TMS as an internal reference. Optical rotations were measured with a JASCO DIP 4 polarimeter. X-band ESR spectra were recorded on a JEOL ES-SCXA spectrometer using frozen-solution samples. Cyclic voltammetric measurements were carried out on dimethyl sulfoxide solutions (1×10^{-3} M complex, 0.1 M Bu_4NBF_4) by using a FUSO HECS 321B potential sweep unit at 24 °C. A glassy carbon, a platinum wire, and an Ag/Ag^+ (Ag/0.01 M $AgNO_3$) electrode were used as the working, auxiliary, and reference electrodes, respectively. The ferrocene/ferrocenium couple was observed at +0.17 V vs. Ag/Ag^+. Conductivity measurements of dimethyl sulfoxide, methanol, and dichloromethane solutions were carried out with a Toa CM-6A conductivity meter. The concentrations of the solutions were approximately 10^{-3} M.

Results and Discussion

Preparation and Characterization of the Complexes. Oxovanadium(IV) complexes of quadridentate Schiff base ligands derived from 1,2-diamines and salicylaldehyde or its derivatives have been extensively studied.[11] These complexes exhibit a tendency to retain five-coordinate square-pyramidal geometry even in donor solvents. However, introduction of electronegative groups in the aromatic ring often leads to a six-coordinate polymer, in which an infinite chain of molecules connected by ···V=O···V=O··· bonds exists.[12] It is known that five-coordinate species are blue or green in color, while six-coordinate complexes are orange or red. We prepared a series of VO(5-Xsal-(*RR*)-chxn) (Xsal=NO_2sal, Brsal, Clsal, sal, MeOsal) complexes simply by mixing solutions of vanadyl sulfate and the Schiff base ligands. We assign the green complexes (Xsal=Brsal, Clsal, sal, MeOsal) to a five-coordinate square pyramidal geometry and the orange VO(5-NO_2sal-(*RR*)-chxn) complex to a chain structure. The IR spectra support the assignments; the orange complex (Xsal=NO_2sal) shows the V=O stretching at a lower frequency (947 cm^{-1}) than those of the other complexes (985—992 cm^{-1}). The reduction in the V=O stretching frequency in VO(5-NO_2sal-(*RR*)-chxn) is attributable to the weakening of the V=O bond by linking ···V=O···V=O··· bonds. A low V=O stretching frequency has been reported for several complexes such as VO(5-NO_2salen)[12] (5-NO_2salen=*N,N'*-di(5-nitrosalicylidene)ethylenediamine) and VO-(salpn)[13] (salpn=*N,N'*-disalicylidene-1,3-propanediamine), and a polymeric, chain structure has been shown by the X-ray method for the latter complex. Other Schiff base-oxovanadium(IV) complexes were prepared and characterized in the same way.

V^VO(salen)Y (Y=Cl, ClO_4) has been previously prepared either by reaction of $VOCl_3$ with the Schiff base ligand in carbon tetrachloride[14] or by the addition of perchloric acid to an acetonitrile solution of $V^{IV}O$(salen) under aerobic conditions.[15] Neither method gives a pure product in a satisfactory yield. We prepared V^VO(Schiff base)Y (Y=Cl, ClO_4, NO_3) in a reasonable yield (50—90%) by oxidizing $V^{IV}O$(Schiff base) with $(NH_4)_2Ce(NO_3)_6$ in acetonitrile followed by the addition of HY. The complexes are stable in most organic solvents, but decompose rapidly in neutral or basic aqueous solutions. They are fairly stable in acidic aqueous solutions; for example, the absorption spectrum of V^VO(sal-(*R*)-pn)Cl in 0.05 M HCl changes gradually over a period of hours.

The molecular structure of $V^VO(salen)ClO_4$ has been determined by the X-ray method to have a distorted octahedral coordination with a relatively long (2.456 (3) Å) V–O(perchlorate) distance.[15] All V^VO(Schiff base)ClO_4 complexes prepared in this study can be assigned to the same distorted octahedral structure in the solid state. The analytical data indicate that some of the complexes contain a water molecule. Since water is a stronger ligand than a perchlorate ion, the position trans to the vanadyl O atom might be occupied by a water molecule. However, the infrared spectra of the perchlorate complexes in Nujol mulls suggest that the perchlorate ion is coordinated; splitting of the ClO_4 band around 1100 cm^{-1} is observed, and the patterns are similar to that of $V^VO(salen)ClO_4$.

The V^VO(Schiff base)Y complexes exhibit a strong tendency to retain six-coordination in both donor and nondonor solvents as indicated by the absorption spectra and the conductivity measurements. In a donor solvent Y is replaced by the solvent molecule. The molar conductivities in DMSO and MeOH are in the range expected for a 1:1 electrolyte (Table 2).[16] The absorption spectra of V^VO(sal-(*RR*)-chxn)Y in DMSO are identical irrespective of Y in line with conductivity measurements. On the other hand, the complexes are essentially nonelectrolytes in nondonor solvents such as dichloromethane. Although extensive ion association will occur even at low concentration in CH_2Cl_2 due to the low dielectric constant and poor solvating properties, the date can be used to differentiate between nonionic and ionic species.[17] The absorption spectra of V^VO(sal-(*RR*)-chxn)Y in CH_2Cl_2 are dependent on Y (Y=Cl, $\tilde{\nu}_{max}=16900\ cm^{-1}$; Y=$ClO_4$ and NO_3, $\tilde{\nu}_{max}=17400\ cm^{-1}$). Thus it is concluded that all of the V^VO(Schiff base)Y (Y=ClO_4, Cl, NO_3) complexes prepared in this study have a six-coordinate structure and that Y coordinates to the vanadium(V)

Table 2. Molar Conductivity in Dimethyl Sulfoxide, Methanol, and Dichloromethane Solutions of Schiff Base-Oxovanadium(V) Complexes at 24 °C (Concentration 10^{-3} M)

Complex	Solvent	Λ_M/S cm^2 mol^{-1}
VO(sal-(*RR*)-chxn)$ClO_4\cdot H_2O$	DMSO	31
	MeOH	93
	CH_2Cl_2	5.2
VO(sal-(*RR*)-chxn)$Cl\cdot 3H_2O$	DMSO	31
	MeOH	76
	CH_2Cl_2	0.18
VO(sal-(*RR*)-chxn)$NO_3\cdot 0.5H_2O$	DMSO	33
	MeOH	87
	CH_2Cl_2	0.11
VO(5-MeOsal-(*RR*)-chxn)$ClO_4\cdot H_2O$	DMSO	31
	MeOH	65
	CH_2Cl_2	5.3
VO(5-NO_2sal-(*RR*)-chxn)ClO_4	DMSO	30
VO(sal-(*R*)-pn)$ClO_4\cdot 0.5H_2O$	DMSO	31
	MeOH	89
	CH_2Cl_2	3.2

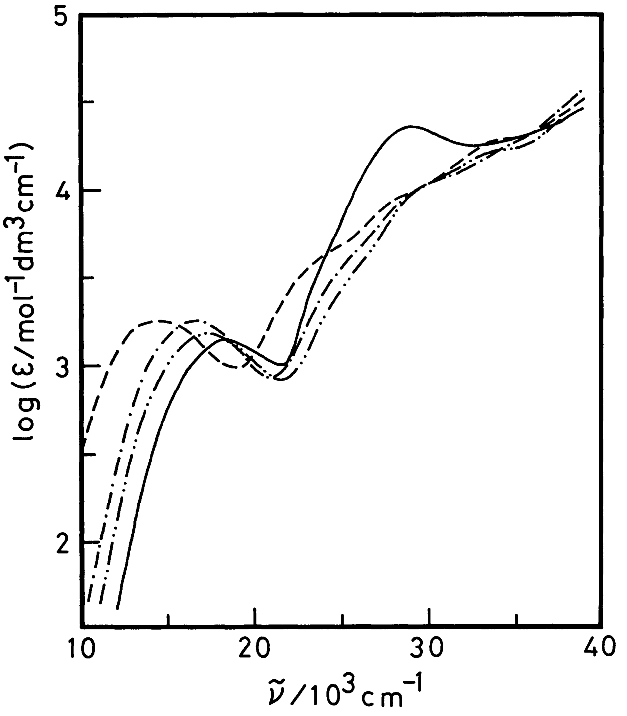


Fig. 1. Absorption spectra of $V^VO(5\text{-Xsal-}(RR)\text{-chxn})ClO_4$ in DMSO, Xsal=NO_2sal (——), Brsal (—•—), sal (—••—), and MeOsal (– – –).

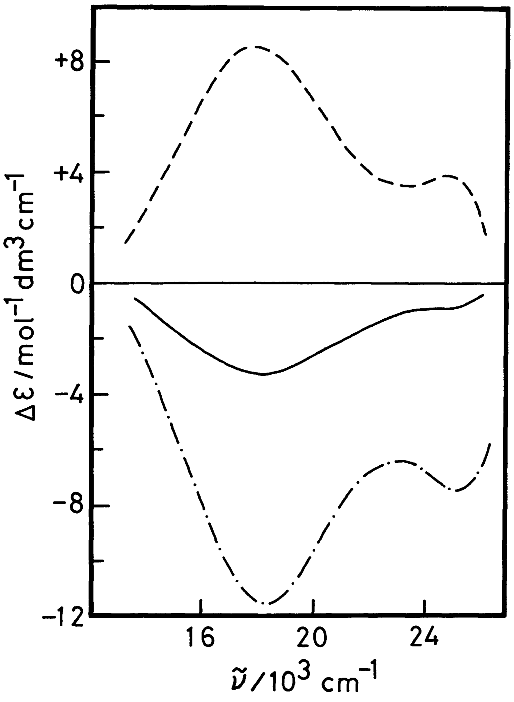


Fig. 2. CD spectra of $V^VO(\text{sal-}(RR)\text{-chxn})ClO_4$ (– – –), $V^VO(\text{sal-}(R)\text{-pn})ClO_4$ (——), and $V^VO(7\text{-Mesal-}(R)\text{-pn})ClO_4$ (—•—) in DMSO.

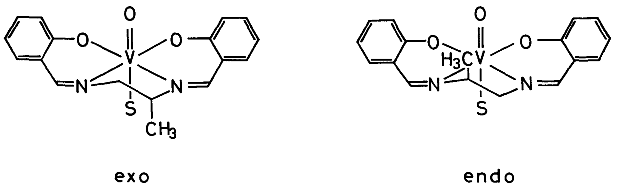


Fig. 3. Two possible geometrical isomers of $[V^VO(\text{sal-}(R)\text{-pn})S]^+$. S denotes a DMSO molecule.

ion in the solid state and in a nondonor solvent. In contrast to V^VO(Schiff base)Y, the $V^{IV}O(5\text{-Xsal-}(RR)\text{-chxn})$ complexes have a five-coordinate square-pyramidal structure except for the complex with Xsal=NO_2sal. The strong absorption of V^VO(Schiff base)Y in the 16600—19800 cm^{-1} region may be assigned to a ligand to metal charge-transfer (LMCT) transition, and such a transition has been observed for other monooxovanadium(V) complexes.[15,18,19] The effect of the X substituent in $V^VO(5\text{-Xsal-}(RR)\text{-chxn})ClO_4$ is reflected in the position of the LMCT band; the energy of the band decreases in the order NO_2sal>sal>Brsal≈Clsal>MeOsal (Fig. 1). The effect should be of electronic origin, since no steric interaction seems to occur. However, the order is different from that observed in electrochemical measurements (vide infra). The V^VO(Schiff base)Y complexes prepared in this study show the V=O stretching frequency in a relatively small range of 960—990 cm^{-1}.

Figure 2 shows the CD spectra of $VO(\text{sal-}(RR)\text{-chxn})ClO_4$, $VO(\text{sal-}(R)\text{-pn})ClO_4$, and $VO(7\text{-Mesal-}(R)\text{-pn})ClO_4$ in DMSO. $VO(\text{sal-}(RR)\text{-chxn})ClO_4$ and $VO(7\text{-Mesal-}(R)\text{-pn})ClO_4$ give CD spectra which are almost mirror images of each other despite the fact that both parent diamines have the same absolute configuration. In $VO(\text{sal-}(RR)\text{-chxn})ClO_4$, the central chelate ring is locked in a λ gauche conformation, while the ring in $VO(7\text{-Mesal-}(R)\text{-pn})ClO_4$ will take a δ gauche conformation to reduce the steric interaction between the methyl substituent on the azomethine carbon and the pn methyl group.[9] The CD spectral pattern of $VO(\text{sal-}(R)\text{-pn})ClO_4$ is similar to that of $VO(7\text{-Mesal-}(R)\text{-pn})ClO_4$, however, the intensity is very small compared with the latter; probably the former complex in solution is in an equilibrium mixture of the conformational isomers (δ and λ) with a small preference of the δ form. Similar relationships among the CD spectra have been reported for the corresponding oxovanadium(IV) complexes, VO(sal-(SS)-chxn), VO(sal-(S)-pn), and VO(7-Mesal-(S)-pn).[9]

For $V^VO(7\text{-Mesal-}(R)\text{-pn})Y$ and $V^VO(\text{sal-}(R)\text{-pn})Y$, two geometrical isomers are possible with respect to the mutual disposition of the pn methyl group and the V=O group (Fig. 3). The ^{1}H NMR spectra indicate the existence of two isomers; $VO(\text{sal-}(R)\text{-pn})ClO_4$ in DMSO-d_6 shows two doublet methyl signals due to the pn moiety at 1.39 and 1.50 ppm in a relative ratio of

1:4, while VO(7-Mesal-(*R*)-pn)ClO_4 in DMSO-d_6 at 1.15 and 1.34 ppm in a ratio of 1:17. An isomer which shows the methyl doublet signal at a higher magnetic field can be assigned as the endo isomer on the basis of the magnetic anisotropy of the V=O group. Distributions of the isomers seem to be related with the steric crowding involved in the isomers. The *endo* isomer, in which the methyl group is situated near the oxo ligand and the steric crowding is larger than in the *exo* isomer, is formed less abundantly. Attempts to separate the isomers by fractional crystallization and by column chromatography were unsuccessful. A similar isomerism has been observed for [V^VO(sal-L-ala)(OCH_3)(CH_3OH)] (sal-L-ala=*N*-salicylidene-L-alaninate).[20]

Electrochemistry. Electrochemistry is very useful for examining electronic effects of substituents on the ligand in metal complexes. The electrochemical measurements of a series of $V^{IV}O$(5-Xsal-(*RR*)-chxn) complexes are precluded by their low solubility in most solvents especially in the case of Xsal=NO_2sal. We could obtain cyclic voltammograms of the corresponding vanadium(V) complexes. The data for V^VO(5-Xsal-(*RR*)-chxn)ClO_4 in DMSO with 0.1 M tetrabutylammonium tetrafluoroborate vs. Ag/Ag^+ (0.01 M) are summarized in Table 3. The complexes show a reversible reduction wave (based on peak height ratio and peak potential separation) in the range of +0.35 V to −0.01 V (Fig. 4). The wave is assignable to the V^{5+}/V^{4+} couple by comparison with the electrochemical data for VO(salen) in the same solvent.[21] In Fig. 5, the $E_{1/2}$ values were plotted as a function of the Hammett σ_p parameter for the X substituent in V^VO(5-Xsal-(*RR*)-chxn)ClO_4. The Hammett para parameter was chosen because the X substituent on the ligand is para to the salicylaldehyde oxygen donor atom. A linear relationship indicates that the electronic effect of a substituent is transmitted through the ligand to the metal in these complexes. As the X substituent becomes more electron-withdrawing (Xsal=MeOsal<sal<Brsal<NO_2sal) the $E_{1/2}$'s are shifted in the anodic direction; the oxovanadium(V) complexes become easier to reduce. An extended ligand π system facilitates this process.

It has been shown that reduction potentials of *cis*-dioxomolybdenum(VI) complexes with tridentate Schiff base ligands correlate well with the electronic effects of the substituents as measured by Hammett substituent effects.[22]

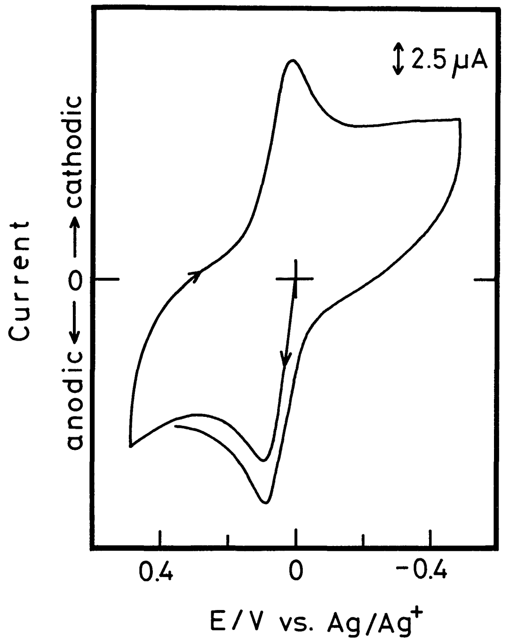


Fig. 4. Cyclic voltammogram of V^VO(sal-(*RR*)-chxn)ClO_4 in DMSO at 24 °C (1.0×10^{-3} M complex; 0.1 M Bu_4NBF_4; scan speed 200 mV s^{-1}; working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, Ag/Ag^+).

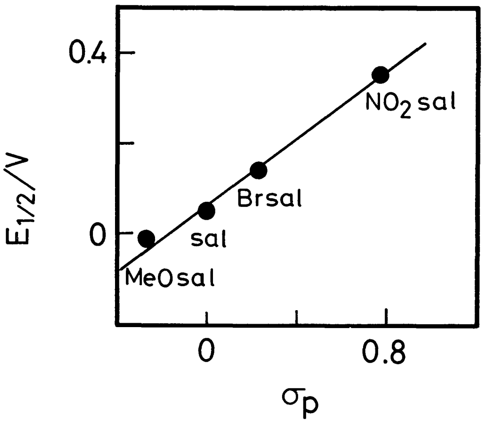


Fig. 5. Plot of the $E_{1/2}$ values vs. the Hammett σ_p for V^VO(5-Xsal-(*RR*)-chxn)ClO_4 (Xsal=NO_2sal, Brsal, sal, MeOsal).

Table 3. Electrochemical Data of V^VO(5-Xsal-(*RR*)-chxn)ClO_4 (vs. Ag/Ag^+) at 24 °C[a]

Xsal	Substituent parameter/σ_p	E_{pa}/V	E_{pc}/V	ΔE_p/mV	$E_{1/2}$/V[b]
NO_2sal	+0.78	+0.38	+0.32	60	+0.35
Brsal	+0.23	+0.17	+0.10	70	+0.14
Sal	0	+0.085	+0.015	70	+0.05
MeOsal	−0.27	+0.03	−0.04	70	−0.01

a) By cyclic voltammetry in dimethyl sulfoxide containing 0.1 M Bu_4NBF_4 at a glassy carbon electrode with a scan rate of 200 mV s^{-1}. b) For a reversible system, the average of the peak potentials corresponds to the polarographic half-wave potential, $(E_{pa}+E_{pc})/2=E_{1/2}$.

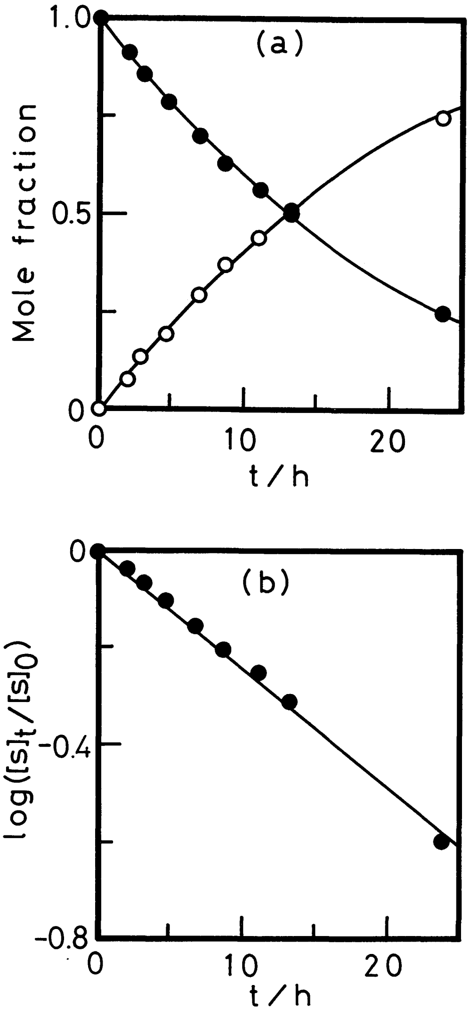


Fig. 6. Oxidation of methyl phenyl sulfide (4.0×10^{-2} M) by 1-methyl-1-phenylethyl hydroperoxide (0.4 M) with the $V^{V}O$(3-MeOsal-(*RR*)-chxn)Cl·$3H_2O$ (4.0×10^{-3} M) catalyst in CH_3CN at 25 °C. (a) Reaction profile: ●, sulfide; ○, sulfoxide, and (b) the plot of log ($[S]_t/[S]_0$) vs. reaction time. [S]=sulfide concentration.

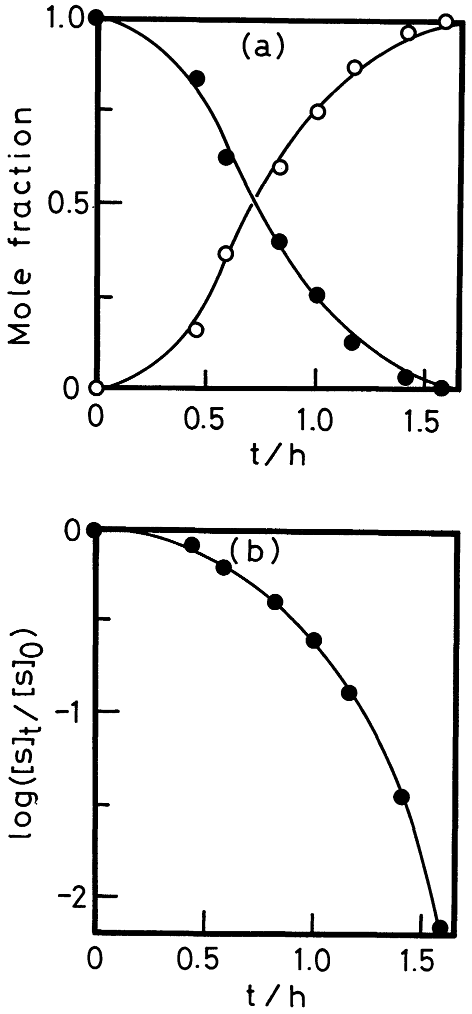


Fig. 7. Oxidation of methyl phenyl sulfide (4.0×10^{-2} M) by 1-methyl-1-phenylethyl hydroperoxide (0.4 M) with the $V^{IV}O$(3-MeOsal-(*RR*)-chxn) (4.0×10^{-3} M) catalyst in CH_2Cl_2 at 25 °C. (a) Reaction profile: ●, sulfide; ○, sulfoxide, and (b) the plot of log ($[S]_t/[S]_0$) vs. reaction time. [S]=sulfide concentration.

Catalytic Oxidation of Sulfides. Figure 6(a) shows the reaction profile for the oxidation of methyl phenyl sulfide (4.0×10^{-2} M) with 1-methyl-1-phenylethyl hydroperoxide (CHP, 0.4 M) in acetonitrile catalyzed by $V^{V}O$(3-MeOsal-(*RR*)-chxn)Cl·$3H_2O$ (4.0×10^{-3} M) at 25 °C. With the peroxide in large excess over the sulfide, the oxidation of the sulfide is first order in the sulfide concentration; the plot of log ($[S]_t/[S]_0$) vs. time gave a straight line for at least two half-lives (Fig. 6(b)), where [S] represents the concentration of the sulfide at the subscripted time. The complex does not decompose appreciably during the reaction as indicated by the absorption spectrum. The spectrum of the complex does not change by the addition of the sulfide and the hydroperoxide. A catalytically active species will be a vanadium(V)–CHP complex. In the absence of complex catalyst, the oxidation of the sulfide proceeds very slowly. Dissolved oxygen does not promote the oxidation of sulfides, and the oxidation does not take place in the absence of peroxides.

The reaction profile for the same oxidation catalyzed by $V^{IV}O$(3-MeOsal-(*RR*)-chxn) (4.0×10^{-3} M) is given in Fig. 7(a). The reaction proceeds very slowly in the beginning, and is accelerated in the course of time. The reaction is not first order in the sulfide concentration (Fig. 7(b)). The reaction is much faster than that with the corresponding oxovanadium(V) complex, and the sulfide is oxidized to the sulfoxide almost completely in 100 min.

Figure 8 shows the change in the absorption spectrum obtained at intervals after mixing $V^{IV}O$(3-MeOsal-(*RR*)-chxn) (4.0×10^{-3} M) with a large excess of CHP (0.4 M) in dichloromethane at 25 °C. The spectral change clearly shows that two step reaction occurs. The first step (a) which produces a dark brown

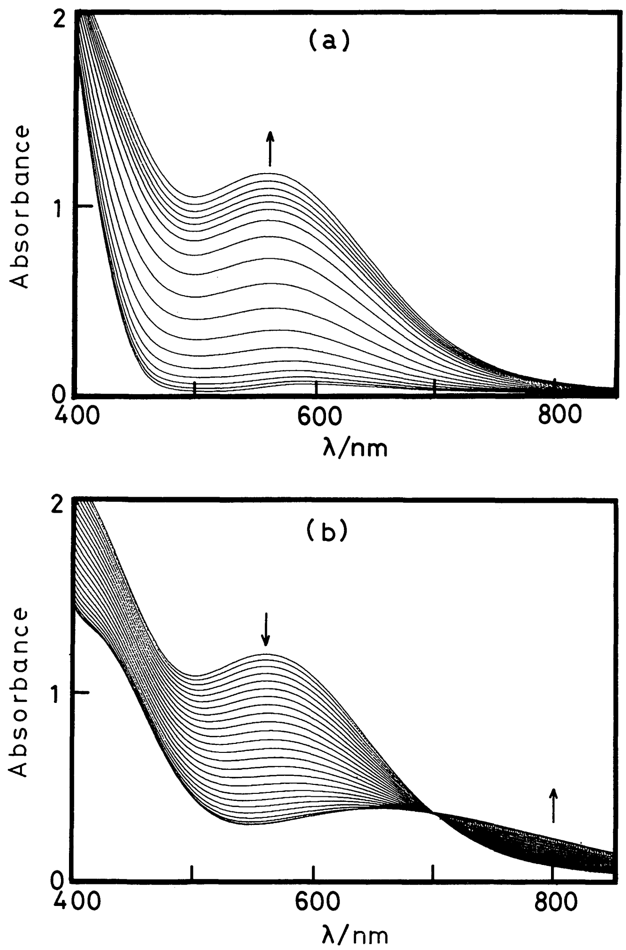


Fig. 8. Change in absorption spectrum of $V^{IV}O$(3-MeOsal-(*RR*)-chxn) (4.0×10^{-3} M) in CH_2Cl_2 in the presence of a large excess of 1-methyl-1-phenylethyl hydroperoxide (4.0×10^{-1} M) at 25 °C (recorded intervals: 10 min). Trends of spectral changes with time are shown by arrows. (a) The spectra recorded from $t=0$ to $t=180$ min. (b) The spectra recorded from $t=210$ to 480 min.

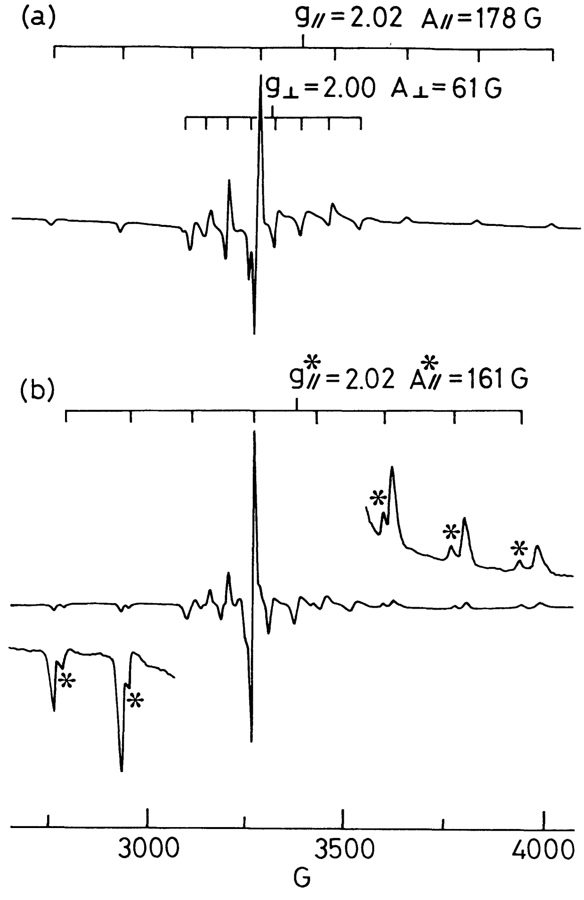


Fig. 9. Change in ESR spectrum of $V^{IV}O$(3-MeOsal-(*RR*)-chxn) by reacting with 15 molar excess of 1-methyl-1-phenylethyl hydroperoxide in CH_2Cl_2 at 20 °C (measured in a frozen glass). (a) Before adding the hydroperoxide. (b) After 3.5 h from adding the hydroperoxide. The peaks with asterisk are due to a newly generated vanadium(IV) species. The values of $g_\perp$ and $A_\perp$ for the generated species could not be determined because of the complicated spectra.

intermediate ($\lambda_{max}=562$ nm) proceeds very slowly in the beginning and is not a simple first order reaction. The intermediate reaches its maximum concentration after ca. 3 h from mixing and then decomposes gradually. The final spectrum is similar to that of $V^{V}O$(3-MeOsal-(*RR*)-chxn)ClO_4. In the second step (b), an isosbestic point is found at 700 nm. The reaction was followed by ESR spectroscopy. $V^{IV}O$(3-MeOsal-(*RR*)-chxn) in frozen dichloromethane gives the ESR spectrum similar to that of $V^{IV}O$(salen).[18,23] Upon mixing with a 15-fold excess of CHP, the intensity of the signal reduces gradually and a new signal appears concomitantly. The pattern of the new signal is similar to that of the original one (Fig. 9). After 24 h, the reaction mixture becomes essentially ESR inactive indicating that all vanadium(IV) species have been oxidized to vanadium(V). The absorption and ESR spectra of $V^{IV}O$(3-MeOsal-(*RR*)-chxn) do not change by the addition of methyl phenyl sulfide. From these observations, we conclude that the brown intermediate vanadium(IV) species is the catalytically active one in the present oxidation of sulfide. This species exists only when the CHP concentration is high. All our efforts to isolate the intermediate were unsuccessful. The structure of the active species remains unknown, but it may be a vanadium(IV)–CHP complex, analogous to the intermediate peroxovanadium(IV) complex formed in the reaction of hydrogen peroxide with aqua(nitrilotriacetato)oxovanadate(IV) and diaquaoxo-(2,6-pyridinedicarboxylato)vanadium(IV) in acidic aqueous solution.[24] The activated organic peroxide in the intermediate will oxidize sulfides.

Several optically active Schiff base-oxovanadium(IV) and -oxovanadium(V) complex catalysts and peroxides were used for the asymmetric oxidation of sulfides and the results are given in Table 4. The oxovanadium(IV) complex catalysts gave much better

Table 4. Asymmetric Oxidation of Sulfides to the Sulfoxides[a]

$$\mathrm{R^1{-}S{-}R^2} \xrightarrow{\text{ROOH/Complex catalyst}} \mathrm{R^1{-}S(O){-}R^2}$$

Entry	Complex catalyst	R^1	R^2	Peroxide[b]	Solvent	Ratio	Temp	Time	Yield[c]	ee[d]
						[V]:[O]:[S][e]	°C	h	%	%(config.)
1	VO(3-MeOsal-(*RR*)-chxn)	Ph	Me	CHP	CH$_2$Cl$_2$	1:10 :10	−20	720	79	40(*S*)
2	VO(3-MeOsal-(*RR*)-chxn)	Ph	Me	CHP	CH$_2$Cl$_2$	1:10 :10	0	120	96	40(*S*)
3	VO(3-MeOsal-(*RR*)-chxn)[f]	Ph	Me	CHP	CH$_2$Cl$_2$	1:12.5:10	0	14	81	41(*S*)
4	VO(3-MeOsal-(*RR*)-chxn)[g]	Ph	Me	CHP	CH$_2$Cl$_2$	1:12 :10	0	19	64[i]	ca. 0
5	VO(3-MeOsal-(*RR*)-chxn)[f]	Ph	Me	CHP	CH$_2$Cl$_2$	1: 9.5:10	0	16	74[i]	42(*S*)
6	VO(3-MeOsal-(*RR*)-chxn)[h]	Ph	Me	CHP	CH$_2$Cl$_2$	1: 9.2:10	0	89	71[i]	38(*S*)
7	VO(3-MeOsal-(*RR*)-chxn)	Ph	Me	CHP	CH$_2$Cl$_2$	1:10 :10	20	37	94	31(*S*)
8	VO(3-MeOsal-(*RR*)-chxn)	Ph	Me	CHP	CH$_2$Cl$_2$	1:10 :10	40	15	75	26(*S*)
9	VO(3-MeOsal-(*RR*)-chxn)	Ph	Me	TBHP	CH$_2$Cl$_2$	1:10 :10	0	120	90	16(*S*)
10	VO(3-MeOsal-(*RR*)-chxn)	Ph	Me	TMHP	CH$_2$Cl$_2$	1:10 :10	0	120	92	7(*S*)
11	VO(3-EtOsal-(*RR*)-chxn)	Ph	Me	CHP	CH$_2$Cl$_2$	1:10 :10	0	120	81	40(*S*)
12	VO(sal-(*RR*)-chxn)	Ph	Me	CHP	CH$_2$Cl$_2$	1:10 :10	0	120	77	21(*S*)
13	VO(3-Bu^{t}sal-(*RR*)-chxn)	Ph	Me	CHP	CH$_2$Cl$_2$	1:10 :10	0	156	70	10(*S*)
14	VO(sal-(*R*)-pn)	Ph	Me	CHP	CH$_2$Cl$_2$	1:10 :10	0	124	74	ca. 0
15	VO(7-Mesal-(*R*)-pn)	Ph	Me	CHP	CH$_2$Cl$_2$	1:10 :10	0	120	89	17(*R*)
16	VO(4-MeOsal-(*RR*)-chxn)	Ph	Me	CHP	CH$_2$Cl$_2$	1:10 :10	0	120	96	15(*S*)
17	VO(3-MeOsal-(*RR*)-chxn)	*p*-Tol	Me	CHP	CH$_2$Cl$_2$	1:10 :10	0	144	71	35(*S*)
18	VO(3-MeOsal-(*RR*)-chxn)	2-Naphthyl	Me	CHP	CH$_2$Cl$_2$	1:10 :10	0	120	76	30
19	VO(3-MeOsal-(*RR*)-chxn)	*p*-Tol	Bu^n	CHP	CH$_2$Cl$_2$	1:10 :10	0	120	70	10(*S*)
20	VO(3-MeOsal-(*RR*)-chxn)	2-Pyridyl	Me	CHP	CH$_2$Cl$_2$	1:10 :10	0	120	82	32
21	VO(5-MeOsal-(*RR*)-chxn)	Ph	Me	CHP	CH$_2$Cl$_2$	1:12.5:10	0	15	87[i]	13(*S*)
22	VO(3-MeOsal-(*RR*)-chxn)ClO$_4$	Ph	Me	CHP	CH$_2$Cl$_2$	1:12.5:10	0	89	93[i]	ca. 0
23	VO(3-MeOsal-(*RR*)-chxn)Cl	Ph	Me	CHP	CH$_3$CN	1:12.5:10	0	258	56[i]	11(*S*)

a) Unless otherwise specified, for a reaction with an oxovanadium(IV)-Schiff base complex catalyst, the complex was stirred with an organic hydroperoxide at room temperature for ca. 30 min, and the resulting dark green solution was cooled to reaction temperature, and then a sulfide was added. b) Peroxide: CHP, 1-methyl-1-phenylethyl hydroperoxide; TBHP, *t*-butyl hydroperoxide; TMHP, 1,1,3,3-tetramethylbutyl hydroperoxide. c) Isolated yield, based on the sulfide unless otherwise stated. d) Based on the optical rotation of the pure enantiomer reported in Refs. 2, 10, and 25, or based on the CD spectral data (see Experimental). e) [V]:[O]:[S] denotes molar ratio of complex catalyst: organic hydroperoxide: sulfide. f) Prior to the addition of the sulfide, the complex catalyst was allowed to react with the hydroperoxide for 4.5 h at room temperature. g) Prior to the addition of the sulfide, the complex catalyst was allowed to react with the hydroperoxide for 20 h at room temperature. h) The entire reaction was carried out at 0 °C. i) Analyzed by high-performance liquid chromatography.

asymmetric induction than the oxovanadium(V) complex catalysts, and we studied the reactions with the oxovanadium(IV) complex catalysts in more detail.

The oxidation reactions proceeded faster if the intermediate had been generated prior to the addition of a sulfide (Entries 3 and 5). This result supports the above assumption that the intermediate is the catalytically active species.

Among three organic hydroperoxides we used, CHP gave higher ee's than the others, and the results may be associated with the steric effect of the phenyl group in CHP. In asymmetric catalytic reactions the importance of the orientation of the phenyl groups has been pointed out.[26,27] The influence of the kind of hydroperoxides on asymmetric oxidation of sulfides with a modified Sharpless reagent has been studied; the enantioselectivity was enhanced by using CHP instead of *t*-butyl hydroperoxide.[2] Although we tried the oxidation of sulfides with triphenylmethyl hydroperoxide as the oxidant in the presence of VO(sal-(*RR*)-chxn), both the complex and the hydroperoxide decomposed rapidly, and only a little amount of the sulfoxide was obtained with no asymmetric induction.

The complex catalysts containing an (*RR*)-chxn moiety gave an (*S*)-sulfoxide, while those containing an (*R*)-pn moiety gave an (*R*)-sulfoxide (Entry 15) or a racemic one (Entry 14). The results can be understood if we assume that the catalytically active species has a conformational chirality similar to that of the added complex. As described before, the central chelate ring of VO(sal-(*RR*)-chxn) is locked in a λ gauche conformation, while that of VO(7-Mesal-(*R*)-pn) will take a δ gauche conformation for steric reasons. VO(sal-(*R*)-pn) in solution is suggested to be an equilibrium mixture of the conformational isomers (δ and λ). The axial disposition of the pn methyl group in VO(7-Mesal-(*R*)-pn) has been confirmed by X-ray analysis.[28] Such a difference in conformational chirality among the complexes should be responsible for the enantioselectivity.

Substitution at the 3-position of the sal-(*RR*)-chxn ligand has a distinct effect on the enantioselectivity of the oxidation of methyl phenyl sulfide. Table 4 shows that the enantioselectivity decreases in the order 3-MeOsal≈3-EtOsal>sal>3-Bu^{t}sal. The results will come from both electronic and steric effects. We tried to study the influence of a substituent at the 5-position in VO(5-Xsal-(*RR*)-chxn) on the oxidation, where the effect will be related only to the electronic one of the X-substituent. Although the experiments were precluded by the low solubilities of the complexes with electronegative groups (Xsal=NO_2sal, Brsal, and Clsal), the VO(5-MeOsal-(*RR*)-chxn) complex catalyst gave a lower ee than VO(3-MeOsal-(*RR*)-chxn) or VO(sal-(*RR*)-chxn). The VO(4-MeOsal-(*RR*)-chxn) complex catalyst also gave a lower ee (Entry 16) than VO(3-MeOsal-(*RR*)-chxn) or VO(sal-(*RR*)-chxn). From these results the effect of substitution at the 3-position of the sal-(*RR*)-chxn ligand is suggested to come mainly from the steric effect, and introduction of a suitable group at the 3-position will improve the stereoselectivity.

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