

Vanadium(IV) and Vanadium(V) Complexes of Salicyladimine Ligands

Kathryn I. Smith, Londa L. Borer,* and Marilyn M. Olmstead†

Department of Chemistry, California State University Sacramento, 6000 J Street, Sacramento, California 95819

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The synthesis and characterization of a V(IV) and a V(V) complex of the salicyladimine ligand system are described. The reaction of salicylaldehyde and 1,3-diaminohydroxypropane with vanadyl sulfate produced a monomer (VOL1) which, upon heating in methanol, crystallized as a V(V) complex (VO₂L1). The reaction of 3-methoxysalicylaldehyde, 1,3-diaminohydroxypropane, and vanadyl sulfate resulted in a binuclear complex held together by hydrogen bonding (VOL2). VOL1 was determined to catalyze the epoxidation of cyclohexene better than VOL2. The synthesis and characterization of VOL1, VOL2, and VO₂L1 are described. The role of each complex as a catalyst for the epoxidation of cyclohexene is investigated. Results indicate that the V(V) complex performs better than either of the V(IV) complexes.

Introduction

Interest in vanadium coordination chemistry over the past decade has accelerated because of its biological importance¹ and its catalytic abilities.² Polymer-bound VO(acac)₂ has been used for the conversion of benzene to phenol³ and cyclohexene to cyclohexene oxide.⁴ Electronegative vanadyl salicyladimine complexes bearing electron-withdrawing substituents have been shown to catalyze cyclohexene epoxidation with moderate enantioselectivities of ~40%.⁵ There are a number of reports of immobilization of vanadium on polystyrene resins.⁶ VO(acac)₂ has recently been microencapsulated to cut down on the amount of leaching during the course of an epoxidation reaction.

In an effort to prepare a polymer-bound vanadyl salicyladimine complex, we have crystallized two new com-

plexes: one a V(IV) complex and the other a V(V) complex. We report the synthesis and characterization of VOL1, VOL2, and VO₂L1 as well as initial reports of the epoxidation reactions.

Experimental Section

Materials. All chemicals were reagent grade and were used as received without further purification.

Ligand and Metal Complex Preparation. The general procedure is that of a Schiff base condensation of salicylaldehyde (1.0 mL, 1.1674 g, 8 mmol) (L1) or 3-methoxysalicylaldehyde (1.2168 g, 8 mmol) (L2) with 1,3-diaminohydroxypropane (0.3609 g, 4 mmol) in methanol. The ligands were not isolated from the methanol solution. Metal complexes were prepared as follows: A solution of vanadyl sulfate trihydrate (0.7501 g, 3.5 mmol) in water was made basic (pH = 13.5) by adding a 0.10 M solution of NaOH. The same product was obtained whether a pH = 5, 9.5, or 13.5 solution was used. The ligand solution, in methanol, was added to the aqueous vanadyl solution and refluxed for 1 h. The solid orange-yellow products were collected by vacuum filtration and washed with dichloroethane.

The orange-yellow product of L1 (VOL1) was heated at 170 °C for several days without change in product color or in the IR spectrum. Anal. Calcd for C₁₇H₁₈N₂O₅V: C, 53.54; H, 4.72; N, 7.35; O, 21.0; V, 13.39. Found: C, 52.95; H, 4.53; N, 7.31; O, 21.28; V, 13.93. IR (KBr, cm⁻¹): 870 (V=O). UV λ_{max}, nm (ε): 362 (5000). Dec at 290–300 °C. Electron paramagnetic resonance (EPR): (g = 1.97, A = 93.4 × 10⁻⁴ cm⁻¹ in acetonitrile solution). μ_{eff} = 2.63 μ_B.

The crystallized vanadium (V) product obtained from boiling VOL1 in methanol was orange-brown in color (VO₂L1). IR (KBr, cm⁻¹): 877 (V–O), 858 (V–O).

* Author to whom correspondence should be addressed. E-mail: borer@csus.edu.

† Department of Chemistry, University of California Davis, One Shields Ave, Davis, CA 95616.

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V(IV) and V(V) Complexes of Salicyladimine

The dull yellow product of L2 was heated at 100 °C for several days. The color changed to a green-brown without a change in the IR spectrum. IR (KBr, cm^{-1}): 959 ($\text{V}=\text{O}$). $\mu_{\text{eff}} = 1.00 \mu_{\text{B}}$. EPR: ($g = 1.94$, $A = 98.1 \times 10^{-4} \text{ cm}^{-1}$ in acetonitrile). Dec at 290–300 °C. The product was crystallized as VOL2.

Epoxidation Reaction. A catalytic amount of each of the vanadyl complexes was added to 30 mL of dichloroethane in a round-bottom flask equipped with a reflux condenser. After 1 h, 2 mL of cyclohexene was added. A 10 μL aliquot was removed and placed in a vial containing pentane and sodium sulfite for reference purposes. *tert*-Butyl hydroperoxide (TBHP) (70%) was slowly added to the catalyst mixture in a 1:1 mole ratio to the cyclohexene over a 30 min period. Cyclohexene oxide formation was monitored by gas chromatography (GC). Alternatively, 12:2 mmol of cyclohexene and TBHP, without solvent, were added to a 10 mL flask. The catalyst was then added in varying amounts from 0.131 to 0.00262 mmol. The reaction mixture was brought to reflux, and samples were taken every 30 min for GC analysis.

X-ray Crystallography. To determine how “free” the hydroxyl group on each of the complexes would be for attachment to Merrifield’s polymer, an effort to crystallize the vanadyl complexes was made. The complex VOL1 was insoluble in most common organic solvents; however, a solution was prepared by boiling the complex in methanol for ~ 1 h. Crystals of suitable quality for X-ray studies were obtained after several days. The resulting dioxovanadium complex is $\text{VO}_2\text{L1}$. Suitable crystals of the oxovanadium complex of L2 (VOL2) were obtained from the slow evaporation of dichloroethane solution.

Data for $\text{VO}_2\text{L1}$ were collected on a Bruker SMART 1000. An orange plate of dimensions $0.29 \times 0.13 \times 0.05 \text{ mm}^3$ was mounted in the 90 K nitrogen cold stream provided by a CRYO Industries low-temperature apparatus on the goniometer head of the Bruker SMART 1000 diffractometer. Diffraction data were collected with graphite-monochromated $\text{Mo K}\alpha$ radiation employing a $0.3^\circ \omega$ scan and approximately a full sphere of data to a maximum 2θ of 63° . An empirical correction for absorption was applied. The structure was solved and refined using SHELXTL 5.1 software. It proved to be a racemic twin; a twin parameter was refined to 0.40(2).

Data for VOL2 were collected on a Siemens P4 diffractometer. A dichroic, green-brown plate of dimensions $0.20 \times 0.16 \times 0.12 \text{ mm}^3$ was mounted in the 130(2) K nitrogen stream provided by a Siemens LT-2 low-temperature apparatus on the goniometer head of the diffractometer. Diffraction data were collected using a Siemens Cu rotating anode and $2\theta-\theta$ scans to a maximum 2θ of 112° . An empirical correction for absorption was applied using the program XABS2. The structure was solved and refined using SHELXTL 5.1 software.

Crystallographic data for the two structures are given in Table 1. Selected bond lengths and angles for $\text{VO}_2\text{L1}$ and VOL2 are given in Tables 2 and 3, respectively.

Results and Discussion

Dimeric vanadium(IV) and monomeric dioxovanadium(V) complexes of *N,N'*-2-propanebis(salicyladimine) have been reported by Murray et al.⁷ This ligand was chosen for this study to determine if the $-\text{OH}$ on the ligand could be used to connect a vanadium complex to a polymer support such as Merrifield’s polymer.

It has been reported that monomeric Schiff base oxovanadium(IV) complexes are green square-pyramidal structures,

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Table 1. Crystallographic Data for $\text{VO}_2(\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_2) \cdot 2\text{H}_2\text{O}$ and $\text{VO}(\text{H}_2\text{O})(\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_5) \cdot 2\text{C}_2\text{H}_4\text{Cl}_2$

	1 ($\text{VO}_2\text{L1}$)	2 (VOL2)
empirical formula	$\text{C}_{10}\text{H}_{17}\text{N}_2\text{O}_6\text{V}$	$\text{C}_{23}\text{H}_{30}\text{Cl}_4\text{N}_2\text{O}_7\text{V}$
fw	312.20	639.23
temp, K	90 (2)	130 (2)
λ , Å	0.710 73	1.541 78
cryst syst	orthorhombic	triclinic
space group	$Pna2_1$	$P\bar{1}$
unit cell dimensions		
a , Å	6.9004(5)	10.6789(10)
b , Å	26.628(2)	11.7717(8)
c , Å	7.2583(6)	12.6972(12)
α , deg	90	66.003(6)
β , deg	90	74.842(7)
γ , deg	90	88.338(7)
V , Å ³	1333.65(18)	1402.0(2)
Z	4	2
ρ_{calc} , $\text{Mg}\cdot\text{m}^{-3}$	1.555	1.514
μ , mm^{-1}	0.768	6.850
$R [I > 2\sigma(I)]^b$ formula	0.0391	0.0391
R (all data)		

Table 2. Selected Bond Lengths and Angles for $\text{VO}_2\text{L1}^a$

About the V Atom				
V(1)–O(1)	1.6268(19)	V(1)–O(4)	1.9193(15)	
V(1)–O(2)	1.6641(18)	V(1)–N(1)	2.158(2)	
V(1)–O(3)	1.8961(18)			
O(1)–V(1)–O(2)	109.76(10)	O(3)–V(1)–N(1)	81.89(7)	
O(1)–V(1)–O(3)	103.18(9)	O(4)–V(1)–N(1)	75.90(7)	
O(2)–V(1)–O(3)	94.70(9)	C(1)–O(3)–V(1)	132.02(15)	
O(1)–V(1)–O(4)	101.73(9)	C(10)–O(4)–V(1)	116.23(14)	
O(2)–V(1)–O(4)	92.13(9)	C(7)–N(1)–V(1)	126.93(17)	
O(3)–V(1)–O(4)	150.14(8)	C(9)–N(1)–V(1)	113.89(14)	
O(1)–V(1)–N(1)	105.19(9)			
O(2)–V(1)–N(1)	144.71(9)			
Hydrogen Bonding				
D–H \cdots A	$d(\text{D}–\text{H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle(\text{DHA})$
N(2)–H(2A) \cdots O(2)#1	0.85(3)	1.88(4)	2.734(3)	177(3)
N(2)–H(2B) \cdots O(4)#2	0.93(3)	1.86(3)	2.763(3)	162(3)
N(2)–H(2C) \cdots O(6)	0.89(5)	1.97(5)	2.806(3)	157(4)
O(5)–H(5A) \cdots O(2)	0.89	1.88	2.696(3)	150.1
O(5)–H(5B) \cdots O(1)#3	0.85	1.90	2.744(3)	172.5
O(6)–H(6A) \cdots O(5)#2	0.83	2.00	2.765(3)	154.5
O(6)–H(6B) \cdots O(5)	0.90	1.89	2.786(3)	173.0

^a Bond lengths in Å and angles in deg.

whereas linear chains ($\text{V}=\text{O}\cdots\text{V}=\text{O}\cdots$) with distorted octahedral geometry are orange.⁸ Thermal reactions of some VO complexes in the solid state show interconversion between monomeric and polymeric forms of the complex.⁹ The VO stretch for a monomer is $\sim 970 \text{ cm}^{-1}$, whereas that of a polymeric form is $\sim 870 \text{ cm}^{-1}$. On the basis of this information, the orange compound prepared using L1 is a polymeric chain of VO, as shown in Figure 1. The magnetic moment, $2.63 \mu_{\text{B}}$, is high for a V(IV) complex; however, spin–orbit coupling or ferromagnetic coupling could explain the results. A V(III) complex (d^2), $\mu_{\text{B}} = 2.83 \mu_{\text{B}}$, does not seem experimentally reasonable as reported by Bhattacharyya et al.¹⁰

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Table 3. Selected Bond Lengths and Angles for VOL2^a

About the V Atom				
V(1)–O(1)	1.606(2)	V(1)–O(2)	1.965(2)	
V(1)–O(6)	1.965(2)	V(1)–N(2)	2.118(3)	
V(1)–N(1)	2.127(3)	V(1)–O(7)	2.299(2)	
O(1)–V(1)–O(2)	101.9(11)	O(1)–V(1)–O(6)	102.47(11)	
O(2)–V(1)–O(6)	85.39(10)	O(1)–V(1)–N(2)	94.89(12)	
O(2)–V(1)–N(2)	162.86(10)	O(6)–V(1)–N(2)	88.14(10)	
O(1)–V(1)–N(1)	95.25(11)	N(2)–V(1)–N(1)	93.14(11)	
O(6)–V(1)–N(1)	162.06(10)	O(2)–V(1)–O(7)	82.02(10)	
O(1)–V(1)–O(7)	173.27(11)	N(2)–V(1)–O(7)	81.46(10)	
O(6)–V(1)–O(7)	83.13(10)	C(1)–O(2)–V(1)	130.2(2)	
N(1)–V(1)–O(7)	79.37(10)			
Hydrogen Bonding				
D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(4)–H(4A)···O(7)	0.83(5)	1.92(5)	2.753(4)	179(5)
O(7)–H(7A)···O(2)#1	0.79(5)	2.16(4)	2.832(3)	143(4)
O(7)–H(7A)···O(3)#1	0.79(5)	2.19(4)	2.841(4)	140(4)
O(7)–H(7B)···O(6)#1	0.87(6)	2.04(5)	2.824(3)	151(5)
O(7)–H(7B)···O(5)13	0.87(6)	2.26(5)	2.900(4)	130(4)

^a Bond lengths in Å and angles in deg.

No change was observed in the IR spectrum or color upon heating; therefore, the polymer was not converted to a monomer. To break the polymeric chain so that the vanadyl complex could be attached to Merrifield's polymer, the orange solid was heated in boiling methanol. Instead of producing a monomeric species, a new complex was produced that was the result of a significant change in the ligand system and the oxidation of V(IV) to V(V). To explain the changes observed, a series of reactions is suggested and shown in Figure 2.

One of the salicylaldehyde ligands was lost, and one imine nitrogen was protonated (Figure 3). The *cis*-dioxovanadium complex that formed is hydrogen bonded via the protonated amine nitrogen and the dioxo group through two water molecules to another complex. This leads to a chainlike association as shown in the packing diagram in Figure 4. The V(V) complex is five coordinate with an NO₄ environment. The V(1)–O(1) and V(1)–O(2) distances of 1.6268(19) and 1.6641(18) Å are somewhat longer than the 1.585(7) Å reported for VO(salen)¹¹ complexes but are shorter than the V(1)–O(3) and V(1)–O(4) bond distances in this complex. They compare favorably with 1.605(2) and 1.647(2) Å reported by Plass et al.¹² and Ligtenberg et al.¹³ for dioxovanadium complexes. Hydrogen bonding of the water molecules to the *cis*-dioxo bonds lengthens the V=O bonds. The complex is a distorted trigonal bipyramid with a bond angle between the oxo groups and the vanadium center of 109.76(10)°; the bond angle between O(4)–V(1)–N(1) is 75.90(7)°, and the angle between O(3)–V(1)–N(1) is 81.89(7)°. The IR spectrum reveals two V=O absorptions at 877 and 858 cm⁻¹ as compared with 926 and 949 cm⁻¹ and 918 and 953 cm⁻¹ for similar dioxo vanadium com-

plexes. The lowering of the IR frequency is the result of hydrogen bonding that involves the *cis*-dioxo groups. A strong, broad NH₃⁺ stretching band in the 3100–2540 cm⁻¹ range is observed in the IR region.

The cyclovoltammogram of the orange polymeric V(IV) complex in DMF solutions of 0.10 M [NBu₄][PF₆] or 0.10 M [NBu₄][BF₄] with a Pt working electrode and a Ag/AgCl reference electrode shows a reversible wave at *E* = 0.553 V or *E* = 0.662 V, respectively. Ion pair differences may be adequate to account for these observed differences.¹⁴ The V(V) complex is very stable, and though it is soluble in polar solvents such as alcohols and DMSO, it could not be reduced in the observable range.

Because the VOL1 complex was polymeric and could not be easily converted into a monomer, the salicyladimine ligand was synthesized with a methoxy group (to introduce steric effects) in the R position (see Figure 1). The resultant complex, VOL2, was orange in color, indicative of a polymeric unit. However, the VO stretch at 959 cm⁻¹ in the IR would suggest that the VO group had not formed a linear polymer. After the complex was heated at 100 °C for several days, the color changed to brown. No change occurred in the IR spectrum; however, changes in the hydrogen bonding probably account for the change in color. Recrystallization from C₂H₄Cl₂ was done because that was the solvent to be used for epoxidation reactions. A single unit of the complex (V1–O7) with one H₂O attached to the vanadium is shown in Figure 5. An association of two units is shown in Figure 6. Selected bond lengths and bond angles are given in Table 3. Rather than a V=O···V=O chain, two individual units are hydrogen bonded together such that the V=O groups are on opposite sides of the dimer. The V=O (V1–O1) distance of 1.606 Å and V(OH₂) distance of 2.299(2) Å are normal for a monomeric [VO]^{IV} species containing the trans unit V^{IV}(=O)–(OH₂), where distances range from ~1.58 to 1.57 Å and from ~2.18 to 2.33 Å, respectively.¹⁵ The two units in the dimer are held together by hydrogen bonding between two water molecules that are located in the sixth position, trans to the V=O in the pseudo-octahedral structure. Each water molecule is hydrogen bonded to the methoxy group on the ligand of the opposite unit. The water molecules exhibit both intermolecular and intramolecular hydrogen bonding, which has also been noted and studied by others.¹⁶

The EPR spectrum in acetonitrile is typical for a VO(IV) complex;¹⁷ however, the room-temperature magnetic moment of 1.00 μ_B would suggest that some exchange is going on between the vanadyl nuclei in the solid state. The UV–visible spectra in DMSO, DMF, and CH₃CN exhibit marked dependence on the coordinating solvent as reported by others.^{18,19} The reduction potential for this complex is 524

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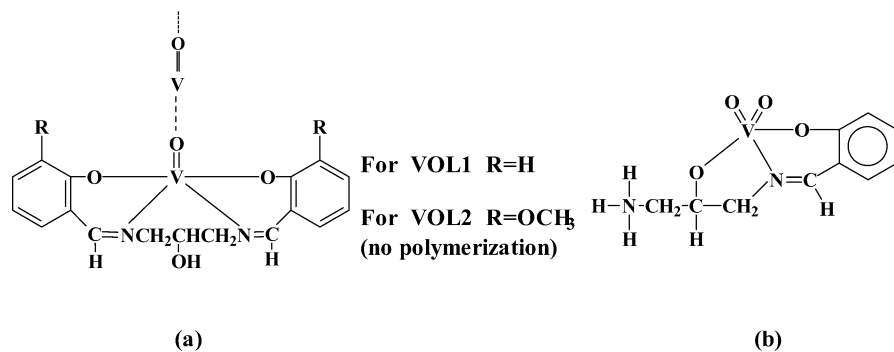


Figure 1. (a) Structures for VOL1 and VOL2. (b) Structure of VO₂L1.

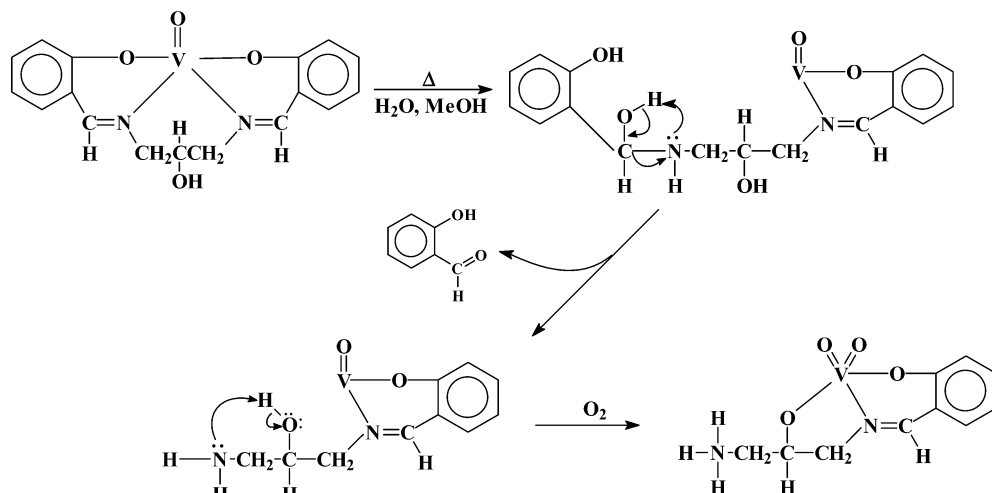


Figure 2. Proposed mechanism for the oxidation of V(IV) to V(V).

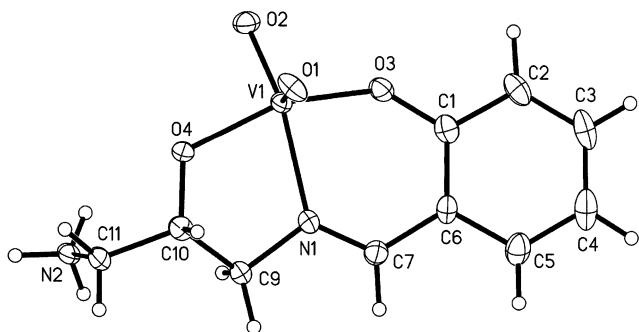


Figure 3. Structure of VO₂(C₁₀H₁₃N₂O₂), VO₂L1, showing thermal ellipsoids at the 50% probability level and the atom-numbering scheme. H atoms are shown at an arbitrary size.

mV with $\Delta E = 84$ mV. Rereduction could not be repeated because precipitation of an unknown complex occurred and there was evidence of chemical degradation.

Epoxidation Reactions. Chromatographic results indicate that when using VOL1 in a solvent, dichloroethane, 90% of the cyclohexene was used up in 200 min; however, only 42% of the epoxide was produced. Side reaction products included cyclohexene-1-ol and cyclohexene-1-one. Results using VOL2 in a solvent system showed that ~80% of the cyclohexene was used up whereas only 25% of the epoxide was formed. The complex hydrogen bonding may have contributed to a reduction in product formation. Boghaei et

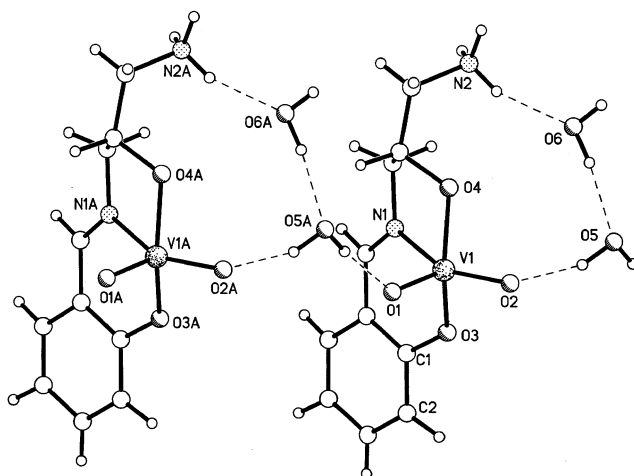


Figure 4. Crystal packing of the V(V) complex, VO₂L1, showing the hydrogen-bonding pattern.

al. have also observed that ligand substitution plays a role in reduction potentials as well as in catalysis reactions.²⁰ A comparison of E^0 values and the percent conversion for VOL1 and VOL2 are given in Table 4. In an attempt to understand the role of solvent and catalyst concentration, the cyclohexene and TBHP were refluxed together. Overall, yields were better than when using a solvent. With a high concentration of catalyst, the reaction proceeded rapidly;

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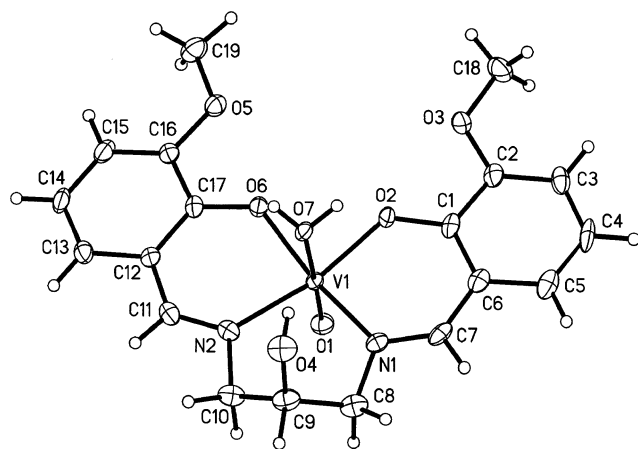


Figure 5. Structure of $\text{VO}(\text{H}_2\text{O})(\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_5)\cdot 2\text{C}_2\text{H}_4\text{Cl}_2$, VOL2, showing thermal ellipsoids at the 50% probability level and the atom-numbering scheme. H atoms are shown at an arbitrary size.

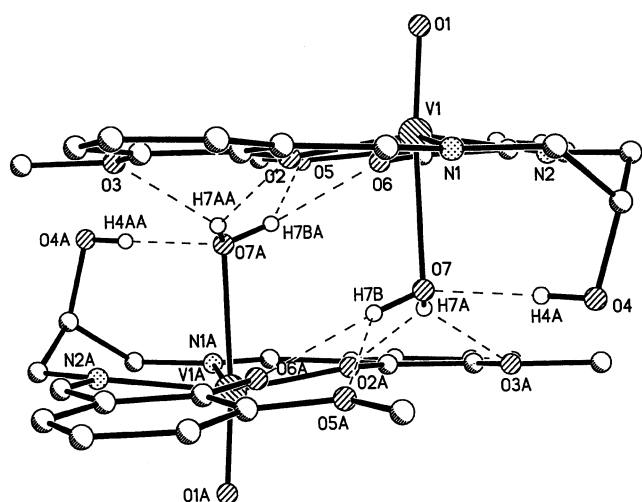


Figure 6. View of the association of two units of VOL2.

Table 4. Catalytic Oxidation of Cyclohexene by VOL1 and VOL2

complex	E^0 (mV) vs AgCl/Ag (ΔE_p (mV))	% conversion
VOL1	553 (80)	42
VOL2	525 (84)	25

however, the yield of epoxide was poor. A large amount of side product, 1,2-cyclohexenediol, was produced. As less catalyst was used, the reaction rate decreased. An optimum amount of catalyst of ~ 0.040 mmol was determined for the conditions chosen. Approximately 50% of the cyclohexene had disappeared and 50% of the epoxide had formed at 180 min, as shown in Figure 7. Proposed mechanisms for epoxidation reactions using TBHP²¹ suggest oxidation of V(IV) to V(V). As would be expected, the V(V) crystallized from the reaction of L1 performed better as a catalyst than did any of the V(IV) complexes. A shorter time of reaction was required and a better yield of product was observed, as shown in Figure 8.

Conclusion

Synthesis of a suitable vanadyl complex to be attached to a polymer support and used to catalyze epoxidation reactions was explored. The V(IV) and the V(V) complexes of the

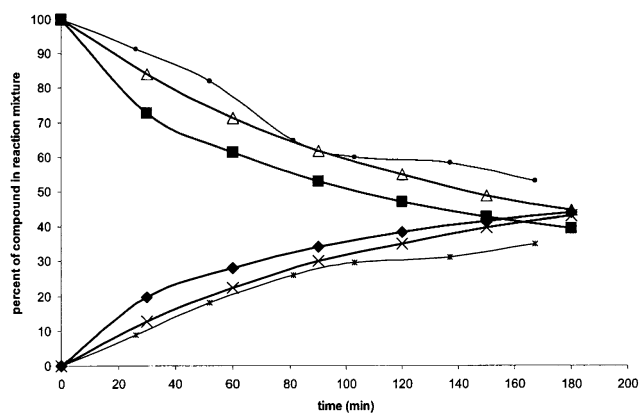


Figure 7. Growth of the epoxide product and decrease in the olefin starting material for three different concentrations of the VOL1 catalyst: (◆) increase in epoxide, high catalyst; (■) decrease in cyclohexene, high catalyst; (×) increase in epoxide, low catalyst; (Δ) decrease cyclohexene, low catalyst; (*) increase in epoxide, very low catalyst; (●) decrease in cyclohexene, very low catalyst.

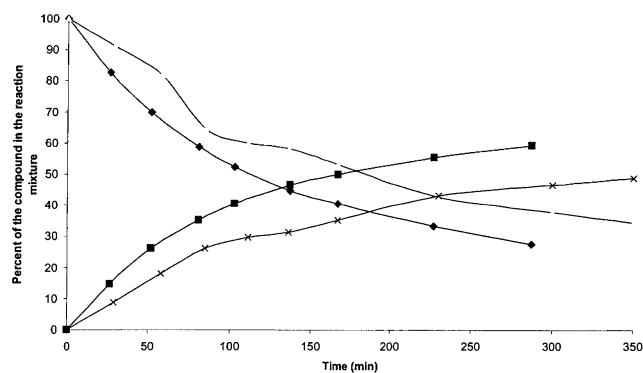


Figure 8. Increase in product and decrease in reactant for the vanadyl(V) reaction compared with the vanadyl(IV) reaction with the same catalyst concentration: (◆) decrease in cyclohexene for V(V) reaction; (■) increase in product for V(V) reaction; (---) decrease in cyclohexene for V(IV) reaction; (×) increase in product for V(IV) reaction.

salicyladimine ligand system did not form stable complexes with the Merrifield's polymer. The uncrystallized orange compound VOL1 is believed to be a polymeric chain of VO on the basis of its color and VO stretch at 870 cm^{-1} in the IR spectrum. An attempt to break the $\text{V}=\text{O}\cdots\text{V}=\text{O}$ polymerization to produce a monomer capable of attaching to the polymer support yielded a five-coordinate V(V) *cis*-dioxovanadium complex, $\text{VO}_2\text{L1}$. $\text{VO}_2\text{L1}$ produced two characteristic IR stretches at 877 and 858 cm^{-1} . Hydrogen bonding via the protonated amine nitrogen and the dioxo group through two water molecules forms a chainlike association (Figure 4) that is also unsuitable to attach to a polymer support.

Because VOL1 was polymeric and attempts to convert it to a monomer did not produce a suitable complex, a methoxy group in the R position was introduced into the ligand to produce steric hindrance. IR analysis showed the $\text{V}=\text{O}$ stretch at 959 cm^{-1} , indicative of a monomeric complex. However, crystallographic analysis revealed an association of two units held together by hydrogen bonding (Figure 6).

(21) Talsi, E. P.; Chinakov, V. D.; Babenko, V. P.; Zamaraev, K. I. *J. Mol. Catal.* **1993**, *81*, 235–254.

V(IV) and V(V) Complexes of Salicylidimine

The VO units face away from each other and are held together by hydrogen bonding through a water molecule. The dimer also exhibits intramolecular hydrogen bonding through the water molecule attached to the hydroxyl group on the bridging diamine as well as to the methoxy group on the opposite unit.

Epoxidation results showed that VO₂L1 performed best as a catalyst. This would be expected because it is believed that V(IV) is oxidized to V(V) during epoxidation reactions with TBHP. VOL1 performed better than VOL2 as a catalyst.

The complex hydrogen bonding in VOL2 is the probable cause of the poor performance.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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