Crystal Structures of [VO(sal-L-ala)(OCH_3)(CH_3OH)] (sal-L-ala=*N*-salicylidene-L-alaninate) and {[VO(sal-L-ala)]$_2$O}$_2\cdot$2CH_2Cl_2, and the Catalytic Activity of These and Related Complexes on Asymmetric Oxidation of Methyl Phenyl Sulfide with *t*-Butyl Hydroperoxide

Kiyohiko NAKAJIMA, Masaaki KOJIMA,† Koshiro TORIUMI, Kazuo SAITO,†† and Junnosuke FUJITA†,*
Institute for Molecular Science, Okazaki National Research Institutes, Myodaiji, Okazaki 444
†Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464-01
††Faculty of Science, International Christian University, Osawa, Mitaka 181

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A reddish brown oxovanadium(V) complex, [V^VO(sal-L-ala)(OCH_3)(CH_3OH)] (**2a**, sal-L-ala=*N*-salicylidene-L-alaninate) was formed by dissolving [$V^{IV}O$(sal-L-ala)(H_2O)] (**1a**) in methanol. Treatment of **2a** with wet dichloromethane yielded deep blue crystals of {[V^VO(sal-L-ala)]$_2$O}$_2\cdot$2CH_2Cl_2 (**3a**). The structures of **2a** and **3a** have been determined by X-ray analyses. Crystal data are: [VO(sal-L-ala)(OCH_3)(CH_3OH)] (**2a**), monoclinic, *C*2, a=19.621(6), b=6.734(1), c=12.059(4) Å, β=117.72(2)° and Z=4. {[VO(sal-L-ala)]$_2$O}$_2\cdot$2CH_2Cl_2 (**3a**), orthorhombic, $P2_12_12_1$, a=19.938(4), b=23.854(5), c=11.526(2) Å, and Z=4. In **2a**, the tridentate sal-L-ala ligand and a methoxide ion occupy the basal positions, and form distorted octahedral geometry around the vanadium(V) ion together with one methanol molecule (V–O distance: 2.384(4) Å) and the oxide ion of oxovanadium(V). The tetranuclear complex (**3a**) consists of two μ-oxo dinuclear vanadium(V) complexes, and each vanadium(V) ion has a distorted octahedral coordination. The Schiff base coordinates equatorially to each vanadium(V) ion, of which one axial site is occupied by O^{2-} and the other is weakly linked to the carboxylate O atom of a nearby Schiff base (V–O distance: 2.34—2.56 Å). Octahedral coordination on each vanadium(V) is achieved by sharing an equatorial O^{2-} ligand. The brown complexes, [VO(sal-L-aa)(OCH_3)(CH_3OH)] (**2**, sal-L-aa=*N*-salicylidene L-amino carboxylate) catalyze the oxidation of methyl phenyl sulfide with *t*-butyl hydroperoxide in dichloromethane at 4 °C to give (*R*)-methyl phenyl sulfoxide with optical yields (e.e.) of 8—14%.

In a previous paper,[1] we reported that optically active tetradentate Schiff base–oxovanadium(IV) complexes catalyze asymmetric oxidation of sulfides into the corresponding sulfoxides with organic hydroperoxides. However, neither the mechanism nor the characterization of useful precursors was discussed in detail. Recently, we found that the oxovanadium(V) complex with a tridentate $^-$O-N-O$^-$-type ligand, [V^VO(dipic)($OOBu^t$)(H_2O)] (H_2dipic=2,6-pyridinedicarboxylic acid, $HOOBu^t$=*t*-butyl hydroperoxide)[2] catalyzes a similar reaction very efficiently.[3] Thus, it seems interesting to examine catalytic activity of oxovanadium(V) complexes with optically active, tridentate $^-$O-N-O$^-$-type Schiff base ligands.

This paper deals with the preparation and characterization of oxovanadium(V) complexes with *N*-salicylidene L-amino carboxylates, X-ray crystal structure analysis of the L-alanine derivatives, and their catalytic activity on asymmetric oxidation of methyl phenyl sulfide with *t*-butyl hydroperoxide.

Experimental

Synthesis. [V^VO(sal-L-aa)(OCH_3)(CH_3OH)] (2) (L-aa=L-ala, L-phe, L-val, and L-leu). These complexes were prepared by a method similar to that of Gillard et al.[4] The procedure is described for the L-ala derivative. The other three complexes were prepared by similar procedures. [$V^{IV}O$(sal-L-ala)(H_2O)][5] (**1a**) (2.11 g, 7.65 mmol) was dissolved in methanol (50 cm^3) to give a reddish brown solution. The solvent was evaporated slowly in a refrigerator to yield brown crystals of [V^VO(sal-L-ala)(OCH_3)(CH_3OH)] (**2a**), which were collected by filtration and air dried. Yield: 1.4 g (57%). Found: C, 44.67; H, 5.02; N, 4.36%. Calcd for $C_{12}H_{16}NO_6V$: C, 44.87; H, 5.02; N, 4.36%. Found: C, 54.12; H, 4.62; N, 3.72%. Calcd for [VO(sal-L-phe)(OCH_3)(CH_3OH)]=$C_{18}H_{20}NO_6V$ (**2b**): C, 54.41; H, 5.07; N, 3.52%. Found: C, 47.89; H, 5.21; N, 4.27%. Calcd for [VO(sal-L-val)(OCH_3)(CH_3OH)]=$C_{14}H_{20}NO_6V$ (**2c**): C, 48.14; H, 5.77; N, 4.01%. Found: C, 49.13; H, 5.60; N, 4.06%. Calcd for [VO(sal-L-leu)(OCH_3)(CH_3OH)]=$C_{15}H_{22}NO_6V$ (**2d**): C, 49.59; H, 6.10; N, 3.86%.

{[VO(sal-L-ala)]$_2$O}$_2\cdot$2CH_2Cl_2 (3a). Complex **2a** (1.4 g, 4.4 mmol) was dissolved in wet dichloromethane (30 cm^3), and the dark blue solution was evaporated to ca. 5 cm^3. The concentrate was allowed to stand in a refrigerator to yield dark blue crystals of **3a**. Yield: 0.9 g (66%).

Crystal Structure Analysis of 2a and 3a. Crystals of [V^VO(sal-L-ala)(OCH_3)(CH_3OH)] (**2a**) and {[V^VO(sal-L-ala)]$_2$O}$_2\cdot$2CH_2Cl_2 (**3a**) were grown by slow evaporation, respectively, from methanol and dichloromethane solutions at room temperature. Crystal data and experimental details are listed in Table 1. A reddish brown prism of **2a** was coated first with paraffin and then with epoxy resin to avoid intensity changes during the data collection. The crystals of **3a** deteriorated when removed from the mother liquor, presumably owing to loss of the solvent of crystallization. A dark blue prism of **3a** was coated with epoxy resin. Intensity data for **2a** and **3a** were collected on a Rigaku AFC-5 and a Rigaku AFC-5R four-circle diffractometer, respectively, by use of graphite monochromatized Mo $K\alpha$ radiation (λ=0.71073 Å). Lattice constants were determined by least-squares calculations based on 2θ values ($22<2\theta<32°$) of 36 reflections for **2a**, and 30 2θ values ($20<2\theta<26°$) for **3a**. The

Table 1. Crystal Data and Experimental Details

Complex	**2a**	**3a**
Formula	$VC_{12}H_{16}NO_6$	$V_4C_{40}H_{36}N_4O_{18}\cdot 2CH_2Cl_2$
Formula weight	321.2	1234.4
Crystal system	Monoclinic	Orthorhombic
Space group	$C2$	$P2_12_12_1$
a/Å	19.621(6)	19.938(4)
b/Å	6.734(1)	23.854(5)
c/Å	12.059(4)	11.526(2)
β/°	117.72(2)	
Z	4	4
V/Å^3	1410.5(8)	5482(2)
D_x/g cm^{-3}	1.51	1.50
μ(Mo $K\alpha$)/cm^{-1}	5.11	5.11
Crystal color	Reddish brown	Dark blue
Crystal habit	Prismatic	Prismatic
Crystal size/mm^3	0.1×0.2×0.3	0.2×0.2×0.35
Scan type	θ–2θ	θ–2θ
$2\theta_{max}$/°	55	50
Reflcns measd	$\pm h, \pm k, +l$	$+h, +l, +k$
No. of reflcns measd	3413	5614
No. of reflcns obsd $[|F_o|>3\sigma(|F_o|)]$	1892	2557
R	0.046	0.088
R_w	0.041	0.111
Weighting scheme	$w=[\sigma_{count}^2+(0.015|F_o|)^2]^{-1}$	$w=[\sigma_{count}^2+(0.020|F_o|)^2]^{-1}$

structures were solved by the direct method (MULTAN 78)⁶⁾ and refined by the block-diagonal least-squares method for **2a**, and by the full-matrix least-squares method for **3a**. The absolute configuration of the structures was assigned on the basis of the known configuration of the L-alanine moiety. The reason for the rather high R-value of **3a** (R=0.088, R_w=0.111) will be discussed later. Atomic scattering factors and anomalous scattering corrections were taken from Ref. 7. The final atomic parameters are listed in Table 2. All the calculations were carried out on a HITAC M-680 computer at the Computer Center of Institute for Molecular Science using the Universal Crystallographic Computation Program System UNICS-III⁸⁾ for **2a** and RADIEL⁹⁾ for **3a**. Lists of observed and calculated structure factors, anisotropic thermal parameters for nonhydrogen atoms, and the coordinates of hydrogen atoms, and the ORTEP drawings of crystal structures are deposited at the office of the Chemical Society of Japan (Document No. 8861).

Reactions. Reaction of 3a with Organic Hydroperoxide. To a dichloromethane solution of **3a** was added ten times molar quantity of 1-methyl-1-phenylethyl hydroperoxide (73%). The color of the solution changed immediately from deep blue to reddish brown. Hexane was added to this solution slowly, and the mixture was allowed to stand in a refrigerator to yield brown crystals (**4a**). Complex **4a** is unstable both in solution and in the solid state. When *t*-butyl hydroperoxide was used instead of 1-methyl-1-phenylethyl hydroperoxide, a similar color change occurred but the product was not isolated because of its high solubility in common organic solvents.

Oxidation of Methyl Phenyl Sulfide by *t*-Butyl Hydroperoxide with a Catalytic Amount of 2. To a dichloromethane solution (10 cm^3) of **2** (0.1 mmol) were added methyl phenyl sulfide (1.0 mmol) and *t*-butyl hydroperoxide (80%, 1.0 mmol), and the mixture was kept at 4 °C. After 5.5—8 h, the solvent was removed under reduced pressure, and the residue was extracted with diethyl ether. The solvent was evaporated off, and methyl phenyl sulfoxide was isolated from the resulting oil. It was purified by column chromatography on silica gel (ϕ 1.0 cm×10 cm, eluent: ethyl acetate–cyclohexane (1:1 (v/v)). The enantiomeric excess (e.e.) was determined on the basis of the reported optical rotation of the pure enantiomer.¹⁰⁾

Spectroscopic Measurements. ^{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. Absorption spectra were recorded on a Hitachi U-3400 spectrophotometer.

Results and Discussion

Characterization and X-Ray Analysis of the Complexes. [V^VO(sal-L-ala)(OCH_3)(CH_3OH)]: The bluish-gray oxovanadium(IV) complexes (**1**) with the general formula of VO(sal-aa)(H_2O) were prepared by Theriot et al. and characterized as a square pyramidal complex with an aqua ligand at the basal site.⁵⁾ Recently, this structure was confirmed by X-ray analysis on the L-alanine derivative.¹¹⁾ Gillard et al.⁴⁾ obtained brown complexes (**2**) from methanol solutions of the bluish-gray complexes (**1**) (Scheme 1). They assigned **2** to monomeric oxovanadium(V) species with the formula [V^VO(sal-aa)(OCH_3)(CH_3OH)], the oxidizing agent being suggested to be atmospheric oxygen. The assignment was confirmed by the present X-ray structure determination on [V^VO(sal-L-ala)(OCH_3)(CH_3OH)] (**2a**). Complex **2a** was prepared from [$V^{IV}O$(sal-L-ala)(H_2O)] by a method similar to that of Gillard et al.⁴⁾ without any particular oxidizing agent.

Figure 1 shows a perspective view of **2a**. Selected bond distances and angles are listed in Tables 3 and 4.

Table 2. Atomic Coordinates ($\times 10^4$; for *V* of **2a** $\times 10^5$) and Equivalent Isotropic Temperature Factors for **2a** and **3a**[a)]

Atom	*x*	*y*	*z*	$B/\text{Å}^2$
	(a) [VO(sal-L-ala)(OCH_3)(CH_3OH)] (**2a**)			
V(1)	17357(4)	0(19)	23234(8)	3.2
O(1)	1860(2)	840(5)	3627(3)	4.7
O(2)	2749(2)	−210(6)	2618(3)	4.0
O(3)	669(2)	−865(4)	1640(3)	3.6
O(4)	1445(2)	2187(5)	1392(3)	4.3
O(5)	−190(2)	−3149(5)	1489(3)	4.7
O(6)	1499(2)	−1642(6)	426(3)	4.1
N(1)	1843(2)	−2996(5)	2853(3)	2.8
C(1)	3273(2)	−1639(8)	2908(4)	3.2
C(2)	3981(3)	−1230(9)	2936(5)	4.6
C(3)	4511(3)	−2695(9)	3184(5)	5.1
C(4)	4367(3)	−4659(11)	3390(5)	5.3
C(5)	3684(3)	−5068(11)	3381(4)	4.2
C(6)	3126(3)	−3605(7)	3151(4)	3.2
C(7)	2414(3)	−4160(7)	3135(4)	3.1
C(8)	1190(3)	−3685(10)	4127(5)	5.4
C(9)	1137(3)	−3817(7)	2834(5)	3.3
C(10)	473(3)	−2569(7)	1911(4)	3.1
C(11)	1027(3)	2609(9)	105(6)	5.8
C(12)	1965(3)	−2015(11)	−155(6)	6.2
	(b) {[VO(sal-L-ala)]$_2$O}$_2$·2CH_2Cl_2 (**3a**)			
V(11)	1087(2)	6293(2)	825(4)	3.6
V(21)	1910(2)	7381(2)	667(4)	3.8
V(31)	−464(2)	8025(2)	2763(4)	3.9
V(41)	375(2)	7727(2)	5253(4)	4.1
O(1)	1461(7)	6823(7)	−82(13)	3.7
O(2)	168(7)	8038(7)	3868(13)	4.3
O(11)	1697(8)	5897(7)	1085(14)	4.6
O(12)	1293(7)	6842(7)	2080(14)	3.7
O(13)	1116(8)	7187(7)	3821(13)	4.1
O(14)	581(10)	5842(7)	−86(14)	5.1
O(21)	2283(9)	7714(7)	−370(16)	5.5
O(22)	1145(8)	7868(7)	759(14)	4.1
O(23)	501(9)	8493(7)	1695(15)	4.7
O(24)	2586(8)	6970(7)	1208(13)	4.6
O(31)	−1104(9)	7709(8)	3311(14)	5.5
O(32)	−72(7)	7376(7)	2029(12)	3.3
O(33)	146(8)	6861(7)	490(14)	4.4
O(34)	−746(8)	8765(7)	2777(15)	4.6
O(41)	−22(9)	8102(10)	6210(15)	6.4
O(42)	1257(9)	8057(7)	5337(16)	5.2
O(43)	2272(10)	8090(8)	6009(18)	6.4
O(44)	−167(7)	7106(7)	5198(15)	4.6
N(11)	491(11)	5991(9)	2214(17)	4.6
N(21)	2081(9)	7884(8)	2138(15)	3.4
N(31)	−850(9)	8038(9)	1169(16)	4.0
N(41)	854(9)	7261(9)	6555(15)	3.7
Cl(11)	495(13)	4551(7)	5895(14)	14.5
Cl(12)	−662(9)	4893(8)	4997(18)	12.4
Cl(21)	6490(12)	3775(12)	5655(22)	19.6
Cl(22)	6577(15)	4125(18)	7937(25)	27.2
Cl(31)	7163(44)	5148(26)	5280(86)	18.5
Cl(32)	7552(47)	4088(54)	6830(78)	34.7
Cl(41)	7678(49)	4765(68)	9805(77)	29.5
Cl(42)	8135(30)	4622(25)	7570(44)	19.2
C(10)	1009(11)	6813(10)	3131(21)	2.8
C(11)	591(14)	6321(12)	3338(24)	5.0
C(12)	939(16)	5900(13)	4238(30)	7.4
C(13)	92(13)	5546(11)	2188(23)	4.1
C(14)	−28(15)	5186(13)	1176(28)	6.2
C(15)	−375(15)	4668(12)	1380(24)	5.3
C(16)	−441(21)	4307(17)	456(37)	9.7
C(17)	−199(16)	4456(14)	−530(29)	6.6
C(18)	116(15)	4917(13)	−837(27)	5.9
C(19)	265(13)	5361(12)	21(24)	4.6
C(20)	1060(15)	8243(12)	1561(24)	4.6
C(21)	1661(13)	8352(11)	2206(22)	4.0
C(22)	1996(16)	8880(14)	1722(30)	7.2
C(23)	2463(12)	7769(10)	3075(21)	3.7
C(24)	2784(13)	7260(12)	3153(23)	4.4
C(25)	3094(15)	7072(13)	4114(28)	6.4
C(26)	3442(15)	6565(14)	4348(29)	6.8
C(27)	3449(15)	6201(13)	3471(26)	5.3
C(28)	3192(12)	6295(11)	2462(24)	4.4
C(29)	2872(13)	6837(11)	2325(24)	4.5
C(30)	−118(11)	7240(10)	1024(20)	2.8
C(31)	−617(13)	7589(12)	364(22)	5.0
C(32)	−287(14)	7853(12)	−858(26)	5.8
C(33)	−1353(12)	8364(10)	770(22)	3.6
C(34)	−1604(12)	8788(11)	1462(22)	3.8
C(35)	−2203(14)	9026(12)	1035(24)	4.9
C(36)	−2463(15)	9458(13)	1610(27)	6.3
C(37)	−2080(16)	9658(13)	2801(28)	6.7
C(38)	−1524(11)	9432(10)	3099(20)	2.9
C(39)	−1298(12)	8974(10)	2438(20)	3.1
C(40)	1729(16)	7900(12)	6148(25)	5.0
C(41)	1546(12)	7463(11)	6899(22)	4.0
C(42)	2002(18)	6974(16)	6970(34)	9.2
C(43)	564(13)	6891(11)	7207(23)	4.3
C(44)	−115(13)	6668(11)	6985(23)	4.4
C(45)	−426(15)	6288(13)	7793(26)	6.0
C(46)	−1036(18)	6109(14)	7591(31)	7.5
C(47)	−1347(18)	6173(16)	6414(32)	7.7
C(48)	−1075(13)	6525(11)	5638(22)	4.2
C(49)	−447(12)	6773(10)	5945(20)	3.3
C(1)	−175(28)	4448(22)	5110(49)	8.4
C(2)	6478(30)	3564(25)	6968(61)	9.7
C(3)	7360(102)	4675(91)	5877(192)	14.7
C(4)	8164(51)	4518(45)	9293(94)	5.5

a) Equivalent isotropic temperature factors ($B_{eq}=4/3\{\sum_i\sum_j B_{ij}a_ia_j\}$) for noncarbon atoms, and isotropic temperature factors for carbon atoms.

The complex has a distorted octahedral coordination. The tridentate Schiff base ligand and a methoxide ion occupy the basal positions, and one methanol molecule (V–O distance: 2.384(4) Å) coordinates at the position trans to the oxo group. Thus the complex has a V^VO^{3+} core and the oxidizing agent should be atmospheric oxygen. Since oxidation of $V^{IV}O^{2+}$ is reported to form a *cis*-$V^VO_2{}^+$ core preferentially,[12] the present result is quite characteristic. The vanadyl V^V=O distance (1.579(3) Å) is almost the same as that (1.578(3) Å) in [V^{IV}O(sal-L-ala)(H_2O)] (**1a**).[11] The V=O bond length seems to be scarcely influenced by the oxidation of the vanadium ion. The vanadium(V) ion of **2a** deviates by 0.306 Å from the best least-squares equatorial plane towards the vanadyl O atom. In [V^VO(salen)ClO_4] (H_2salen=*N*,*N*′-disalicylideneethylenediamine), the

Table 3. Selected Bond Lengths (*l*/Å) for **2a** and **3a**

(a) $[VO(sal\text{-}L\text{-}ala)(OCH_3)(CH_3OH)]$ (**2a**)

V(1)-O(1)	1.579(4)	N(1)-C(7)	1.277(6)
V(1)-O(2)	1.856(4)	N(1)-C(9)	1.482(7)
V(1)-O(3)	1.947(3)	C(1)-C(2)	1.401(8)
V(1)-O(4)	1.778(4)	C(2)-C(3)	1.362(8)
V(1)-O(6)	2.384(4)	C(3)-C(4)	1.399(10)
V(1)-N(1)	2.097(4)	C(4)-C(5)	1.364(9)
O(2)-C(1)	1.330(6)	C(5)-C(6)	1.401(8)
O(3)-C(10)	1.300(6)	C(6)-C(1)	1.415(7)
O(4)-C(11)	1.406(7)	C(6)-C(7)	1.437(8)
O(5)-C(10)	1.219(6)	C(8)-C(9)	1.515(9)
O(6)-C(12)	1.409(9)	C(9)-C(10)	1.514(6)

(b) $\{[VO(sal\text{-}L\text{-}ala)]_2O\}_2\cdot 2CH_2Cl_2$ (**3a**)

	n=1	*n*=2	*n*=3	*n*=4
V(*n*1)-O(*n*1)	1.571(17)	1.617(19)	1.611(18)	1.626(19)
V(*n*1)-O(*n*2)	1.994(17)	1.919(16)	1.931(16)	1.929(18)
V(*n*1)-O(*n*4)	1.810(18)	1.781(17)	1.852(17)	1.835(17)
V(*n*1)-N(*n*1)	2.120(21)	2.104(19)	1.992(19)	2.098(19)
O(*n*2)-C(*n*0)	1.34(3)	1.30(3)	1.21(3)	1.38(4)
O(*n*3)-C(*n*0)	1.22(3)	1.27(4)	1.21(3)	1.19(4)
O(*n*4)-C(*n*9)	1.32(3)	1.44(3)	1.27(3)	1.30(3)
N(*n*1)-C(*n*1)	1.53(3)	1.40(3)	1.49(3)	1.52(3)
N(*n*1)-C(*n*3)	1.33(3)	1.35(3)	1.35(3)	1.30(3)
C(*n*0)-C(*n*1)	1.46(4)	1.43(4)	1.51(4)	1.40(4)
C(*n*1)-C(*n*2)	1.60(4)	1.53(4)	1.68(4)	1.48(5)
C(*n*3)-C(*n*4)	1.47(4)	1.38(4)	1.38(4)	1.48(4)
C(*n*4)-C(*n*5)	1.44(4)	1.35(4)	1.41(4)	1.44(4)
C(*n*5)-C(*n*6)	1.38(5)	1.42(5)	1.33(4)	1.31(5)
C(*n*6)-C(*n*7)	1.29(5)	1.33(5)	1.64(5)	1.50(5)
C(*n*7)-C(*n*8)	1.32(5)	1.29(4)	1.28(4)	1.34(5)
C(*n*8)-C(*n*9)	1.48(4)	1.45(4)	1.41(3)	1.43(4)

V(11)-O(1)	1.802(16)	V(21)-O(1)	1.821(16)
V(31)-O(2)	1.791(15)	V(41)-O(2)	1.809(16)
V(11)-O(33)	2.344(17)	V(21)-O(12)	2.412(16)
V(31)-O(23)	2.542(18)	V(41)-O(13)	2.562(16)

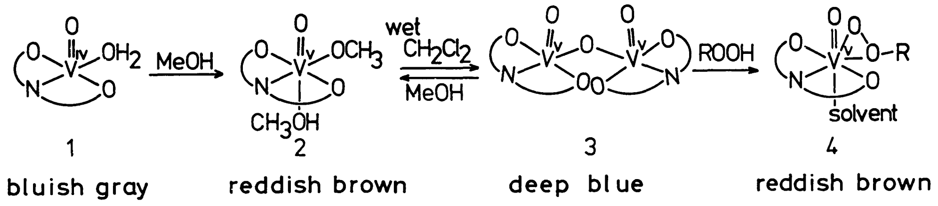
Table 4. Selected Bond Angles (*ϕ*/°) for **2a** and **3a**

(a) $[VO(sal\text{-}L\text{-}ala)(OCH_3)(CH_3OH)]$ (**2a**)

O(1)-V(1)-O(2)	100.4(2)	O(2)-V(1)-N(1)	85.5(2)
O(1)-V(1)-O(3)	99.6(2)	O(3)-V(1)-O(4)	90.8(2)
O(1)-V(1)-O(4)	100.8(2)	O(3)-V(1)-O(6)	76.3(2)
O(1)-V(1)-O(6)	172.9(2)	O(3)-V(1)-N(1)	77.1(1)
O(1)-V(1)-N(1)	95.4(2)	O(4)-V(1)-O(6)	85.2(2)
O(2)-V(1)-O(3)	154.5(2)	O(4)-V(1)-N(1)	161.2(1)
O(2)-V(1)-O(4)	100.6(2)	O(6)-V(1)-N(1)	78.1(2)
O(2)-V(1)-O(6)	82.0(2)		

(b) $\{[VO(sal\text{-}L\text{-}ala)]_2O\}_2\cdot 2CH_2Cl_2$ (**3a**)

	n=1	*n*=2	*n*=3	*n*=4
O(*n*1)-V(*n*1)-O(1)	102.3(8)	103.6(8)	—	—
O(*n*1)-V(*n*1)-O(2)	—	—	106.6(8)	105.1(9)
O(*n*1)-V(*n*1)-O(*n*2)	95.6(8)	96.3(8)	96.7(8)	100.6(9)
O(*n*1)-V(*n*1)-O(*n*4)	100.6(9)	100.4(9)	101.6(8)	100.5(9)
O(*n*1)-V(*n*1)-N(*n*1)	94.9(8)	104.0(8)	93.6(9)	91.7(9)
O(1)-V(*n*1)-O(*n*2)	82.8(7)	94.5(7)	—	—
O(2)-V(*n*1)-O(*n*2)	—	—	92.3(7)	94.9(7)
O(1)-V(*n*1)-O(*n*4)	108.1(8)	97.8(8)	—	—
O(2)-V(*n*1)-O(*n*4)	—	—	101.0(7)	99.5(7)
O(*n*2)-V(*n*1)-N(*n*1)	77.9(7)	74.9(7)	76.4(7)	76.4(7)
O(*n*4)-V(*n*1)-N(*n*1)	85.7(8)	84.8(8)	82.9(8)	82.3(7)
O(1)-V(*n*1)-N(*n*1)	155.3(8)	151.4(7)	—	—
O(2)-V(*n*1)-N(*n*1)	—	—	158.0(8)	162.4(8)
O(*n*2)-V(*n*1)-O(*n*4)	157.8(8)	156.3(8)	153.1(7)	150.3(8)
V(11)-O(1)-V(21)	116.2(8)	V(31)-O(2)-V(41)		141.4(10)



Scheme 1.

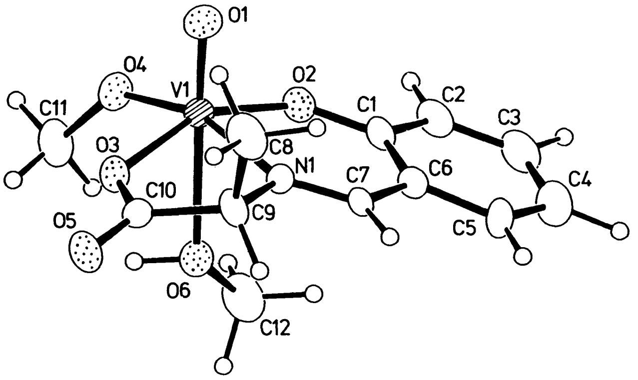
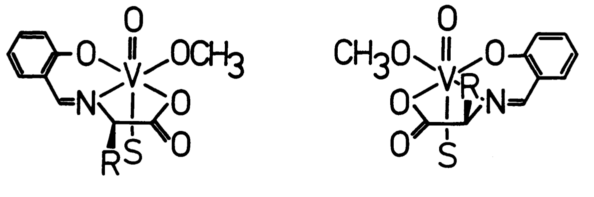


Fig. 1. ORTEP drawing and atom-numbering scheme for [V^VO(sal-L-ala)(OCH_3)(CH_3OH)] (**2a**). Vanadium and oxygen atoms are shown as shaded and dotted circles, respectively.



exo endo

Fig. 2. Two possible geometrical isomers of [V^VO(sal-L-aa)(OMe)(MeOH)], and S denotes a methanol molecule.

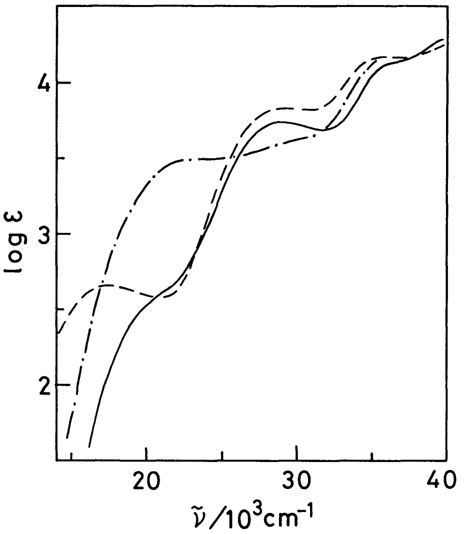


Fig. 3. Absorption spectra of [V^VO(sal-Lala)(OCH_3)(CH_3OH)] (**2a**, ca. 1×10^{-3} mol dm^{-3} in the visible region and ca. 1×10^{-4} mol dm^{-3} in the UV region) in methanol (——), in wet dichloromethane (– – –) to form [VO(sal-L-ala)]$_2$O, and in wet dichloromethane in the presence of a large excess of *t*-butyl hydroperoxide (—·—) to form **4**.

vanadium atom is displaced towards the vanadyl O atom by 0.318 Å from the best salen N_2O_2 least-squares plane, and the V–O (perchlorate) length is relatively long (2.456(3) Å).[13] The vanadyl V^V=O distance of 1.576(3) Å in this complex is nearly the same as that of **2a**, but is shorter by 0.012 Å than the V^{IV}=O distance of [$V^{IV}O$(salen)].[14]

For the [VO(sal-L-aa)(OCH_3)(CH_3OH)] (**2**) complexes, two geometrical isomers are possible with respect to the mutual disposition of the substituent on L-aa and the V=O group (Fig. 2). The crystal of **2a** subjected to the present analysis contains the endo isomer. However, the ^{1}H NMR spectrum of complex **2a** in CD_3OD gives two doublet methyl signals due to the L-ala moiety at δ 1.60 and 1.73 in a relative ratio of 3:4, indicating the existence of two isomers. Since rapid isomerization between the two isomers is very unlikely, the complex obtained by the present synthesis will be a mixture of the two isomers. Attempts to separate the isomers by fractional crystallization were unsuccessful. Other methanolato complexes **2b**—**2d** were assigned to the same structure as **2a**, since the absorption spectra of these complexes are very similar to that of **2a** shown in Fig. 3.

[V^VO(sal-L-ala)]$_2$O·CH_2Cl_2: When the brown complex, **2a** was dissolved in wet dichloromethane, the color of the solution changed immediately from reddish brown to dark blue (Fig. 3), from which the dark blue crystals, **3a** were obtained (Scheme 1). Theriot et al.[15] obtained a green complex by a similar reaction and assigned it as a dimeric vanadium(IV) complex with the formula [$V^{IV}O$(sal-L-ala)(H_2O)]$_2$ on the basis of the data of magnetic susceptibility and molecular weight measurements, the carboxylate oxygen atoms being suggested to bridge the vanadium atoms. However, compound **3a** has the chemical composition of [VO(sal-L-ala)]$_2$O·CH_2Cl_2 and is ESR inactive both in the solid state and in frozen

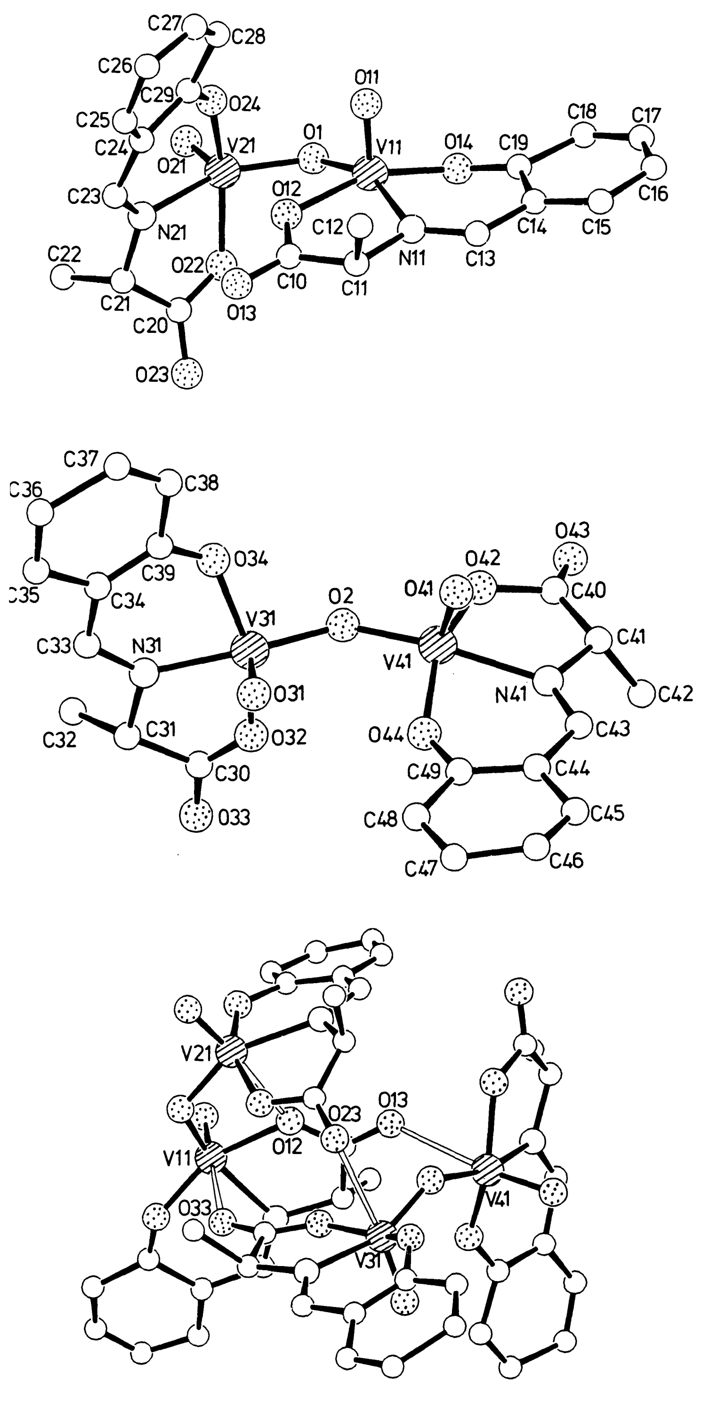


Fig. 4. ORTEP drawings and atom-numbering schemes for **3a-1** (endo form) (a), **3a-2** (exo form) (b), and the tetranuclear unit (**3a**) consisting of **3a-1** and **3a-2** (c). Vanadium and oxygen atoms are shown as shaded and dotted circles, respectively. Open rods indicate weak V–O bonds.

dichloromethane. These facts indicate that the oxidation state of vanadium is +5. The ^{1}H NMR spectrum of **3a** in CD_2Cl_2 exhibits two methyl doublets at δ 1.49 and 1.55 with the same intensity.

The X-ray analysis of **3a** disclosed that two isomeric dimers, **3a-1** and **3a-2** exist in a unit cell together with dichloromethane molecules (Fig. 4). Dimers **3a-1** and **3a-2** are close to each other to form a tetranuclear unit (Fig. 4(c)) and linked by weak bonds between vanadium atoms and carboxylate oxygen atoms of nearby Schiff bases with V–O distances of 2.344(17)—2.562(16) Å (Fig. 4(c)). The geometry around each vanadium atom can be described as a distorted octahedron. The tridentate Schiff base ligand coordinates in the basal plane. The vanadyl O atom occupies an axial site, and the carboxylate O atom of a nearby Schiff base ligand weakly coordinates at the site trans to the oxide ion. The octahedral coordination is completed by sharing an equatorial O^{2-} ligand. The two halves of each dimeric unit have the same geometrical configuration with respect to the disposition of the methyl and V=O groups; **3a-1** consists of two endo isomers while **3a-2** two exo isomers. Each V atom is displaced toward the vanadyl O atom by 0.291—0.363 Å from the equatorial plane. Close contact between O(31) and O(44) in **3a-2** is avoided by the large V(31)-O(2)-V(41) angle (141.4(10)°). In **3a-1**, there is no such close contact around the bridging group, and the V(11)-O(1)-V(21) angle is 116.2(8)°.

The dichloromethane molecules are highly disordered and are continuously distributed along the c-axis in a tunnel structure of the crystal. This structure should be responsible for the loss of solvent of crystallization and also for the large thermal parameters. Thus enough numbers of reflection data were not obtained to determine more accurate structure. An attempt of low temperature measurement was not effective.

Complex **3a** was formed by the treatment of **2a** with wet dichloromethane, but regenerated **2a** on treatment with methanol (Scheme 1). It is to be noted that **3a** is not formed when **2a** is dissolved in anhydrous dichloromethane. Thus the bridging oxygen atom seems to come from water in wet dichloromethane. Brown complex **4a** was obtained by the reaction of **3a** with 1-methyl-1-phenylethyl hydroperoxide in dichloromethane. The complex was unstable both in solution and in the solid state. When *t*-butyl hydroperoxide was used instead of 1-methyl-1-phenylethyl hydroperoxide, a similar color change occurred but the product was not isolated. Figure 3 shows the absorption spectrum of **3a** in the presence of a large excess of *t*-butyl hydroperoxide. Structure determination of **4a** was not achieved because of its instability. Organic peroxide complexes of vanadium(V) with dipic have been prepared and the structure of [VO(dipic)(OOBu^t)(H_2O)] has been determined by the X-ray method.[2] This complex takes a pentagonal bipyramidal structure, the basal positions of which are occupied by two oxygen atoms of the peroxo group, and one nitrogen and two oxygen atoms of the dipic ligand. The peroxide ligand in the complex was

Table 5. Asymmetric Oxidation of Methyl Phenyl Sulfide to the Sulfoxide with *t*-Butyl Hydroperoxide by Complex Catalyst **2** (4 °C)[a)]

Entry	Complex catalyst	Time/h	Yield/%[b)]	e.e./%[c)]	Sulfoxide configuration
1	**2a**	8	50	4	*R*
2	**2b**	8	80	11	*R*
3	**2c**	6	78	14	*R*
4	**2d**	5.5	84	9	*R*

a) All reactions were performed as described in detail in Experimental. Molar ratio of complex catalyst: *t*-butyl hydroperoxide: methyl phenyl sulfide = 1 : 10 : 10. b) Isolated yields, based on the sulfide. c) Based on the optical rotation of the pure enantiomer reported in Ref. 10.

reported to dissociate partially in a $(CD_3)_2CO$ solution by the NMR spectrum. Complex **4a** gives a reddish brown solution when dissolved in dichloromethane, but the color changed to violet brown within a few minutes at room temperature. The ^1H NMR spectrum of **4a** in CD_2Cl_2 shows a singlet methyl signal at δ 1.58 (6H) and multiplet phenyl signals at δ 7.25—7.56 (5H). These signals are identical with those of free 1-methyl-1-phenylethyl hydroperoxide in the same solvent. No signal attributable to the coordinated hydroperoxide was observed in the spectrum. The structure of complex **4a** remains unknown, but the complex seems to contain the peroxide coordinated to the vanadium(V) ion in a similar manner to the above dipic complex, and seems to release the peroxide rapidly on dissolution in dichloromethane. The peroxide complex will be formed only in the presence of a large excess of the peroxide.

The ^1H NMR spectrum of **4a** in CD_2Cl_2 changes within a few days at room temperature. Intensity of the methyl signal due to free 1-methyl-1-phenylethyl hydroperoxide at δ 1.58 becomes weaker and new signals grow gradually at δ 1.55, 2.12, and 2.58, which were assigned to the methyl groups of 2-phenyl-2-propanol, acetone, and acetophenone, respectively. In the absence of complex, such reductive decomposition of the hydroperoxide proceeds much more slowly.

Catalytic Activity of the Complexes. Table 5 shows the results of asymmetric oxidation of methyl phenyl sulfide with *t*-butyl hydroperoxide catalyzed by **2a**—**2d** in CH_2Cl_2. Dissolving **2** in wet dichloromethane yields a deep blue solution of **3**, and the color of the solution changes immediately to reddish brown on the addition of excess *t*-butyl hydroperoxide to form the peroxo complex **4** (Scheme 1 and Fig. 3). The activated peroxide in **4** will oxidize sulfides. For example, methyl phenyl sulfide is oxidized to the sulfoxide in CH_2Cl_2 with *t*-butyl hydroperoxide almost completely in 20 min at room temperature in the presence of a catalytic amount of **2a**. It was found that $[V^VO(dipic)(OOBu^t)(H_2O)]$ is also an excellent catalyst for the same oxidation in acetonitrile; the oxidation was completed in 10 min at room temperature.[3)] On the other hand, the same reaction proceeds very slowly in dichloromethane with the oxovanadium(V) complexes containing tetradentate Schiff bases such as $[V^VO(\text{sal-}(RR)\text{-chxn})X]$ (H_2sal-(*RR*)-chxn=(1*R*,2*R*)-*N*,*N'*-disalicylidene-1,2-cyclohexanediamine, X=ClO_4, Cl, NO_3), where the Schiff base occupies the four basal coordination sites.[16)] Thus, sulfides seem to be oxidized easily only when the vanadium(V) ion can provide a basal coordination site for an organic peroxide. Since the ligand at the site trans to the vanadyl O atom is known to be replaced rapidly by another ligand, a sulfide (substrate) may coordinate at this apical site and be oxidized to the sulfoxide by the activated peroxide.

Recently, Colonna et al.[17)] reported that oxidation of sulfides with *t*-butyl hydroperoxide in the presence of a catalytic amount of an oxovanadium complex containing sal-L-val led to racemic products, the characterization of the complex being not described. When **2** was used as the catalyst, however, (*R*)-methyl phenyl sulfoxide was obtained with an enantiomeric excess (e.e.) of 4—14% (Table 5). The e.e. seems to increase with a decrease in temperature. For example, at −30 °C the e.e. was 8% (*R*) for the same reaction with complex catalyst **2a**.

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