Interconversion between Polymeric and Monomeric Forms of Oxovanadium(IV) Complexes with Tetradentate Schiff Base Ligands Derived from (*R,R*)-2,4-Pentanediamine

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New tetradentate Schiff base−oxovanadium(IV) complexes, [VO{3-Xsal-(*R,R*)-2,4-ptn}] (H$_2${3-Xsal(*R,R*)-2,4-ptn}: *N,N′*-di-3-Xsalicylidene-(*R,R*)-2,4-pentanediamine; X = EtO (ethoxy), MeO (methoxy), and H) were prepared and characterized. Only an orange polymeric form was obtained for the 3-methoxy and nonsubstituted (X = H) complexes. Both orange polymeric (**1**) and green monomeric (**2**) crystals were obtained for the 3-ethoxy substituted complex. X-ray structure analyses of **1** and **2** were carried out. Crystal data: [VO{3-EtOsal-(*R,R*)-2,4-ptn}]·H$_2$O (**1**), VO$_6$N$_2$C$_{23}$H$_{30}$, orthorhombic, *P*2$_1$2$_1$2$_1$, *a* = 13.764(4) Å, *b* = 21.544(4) Å, *c* = 7.682(5) Å, *Z* = 4; [VO{3-EtOsal-(*R,R*)-2,4-ptn}] (**2**), VO$_5$N$_2$C$_{23}$H$_{28}$, orthorhombic, *P*2$_1$2$_1$2$_1$, *a* = 10.393(2) Å, *b* = 22.278(2) Å, *c* = 9.886-(2) Å, *Z* = 4. The orange crystals (**1**) have water of crystallization, and the complexes take a polynuclear linear chain structure (···V=O···V=O···) with a six-membered N−N chelate ring in a chair form. The green crystals (**2**) have no water of crystallization, and the complexes take a mononuclear square-pyramidal structure with a six-membered N−N chelate ring in a flattened boat form. Upon heating at 170 °C for 10 min, orange **1** turned to green **2**, which reverted to orange **1** by suspension in water−acetonitrile. Mechanism of the interconversion between the polymeric and monomeric forms is discussed on the basis of their crystal structures.

Introduction

Most oxovanadium(IV) complexes with a tetradentate Schiff base ligand like salen (H$_2$salen: *N,N′*-disalicylideneethylenediamine) take green monomeric structures with square-pyramidal coordination geometry. However, orange polynuclear linear chain structures (V=O···V=O···)[1,2] and orange octahedral structures with a weak coordination of a solvent molecule[3] are observed in the solid state for the Schiff base−oxovanadium-(IV) complexes which have a six-membered N−N chelate ring. These complexes take a distorted-octahedral coordination with a terminal oxygen atom (V=O) of the adjacent molecule (V···O distance: 2.213(9) Å for [VO(salpn)] (H$_2$salpn: *N,N′*-disalicylidenepropanediamine)[1] or a solvent molecule (V···solvent distance: 2.230(3) Å for [VO(salpn)(DMSO)] (DMSO = dimethyl sulfoxide))[3] at the sixth position trans to the oxo atom. The six-membered chelate ring takes a chair form in these complexes. When bulky substituents are introduced into a six-membered N−N chelate ring, one may obtain both green monomeric and orange polymeric forms according to the inter- and intramolecular steric repulsions caused by the substituents.

Recently, interconversion between monomeric and polymeric forms of [VO{sal-(*R,R*)-stien}] (H$_2${sal-(*R,R*)-stien}: *N,N′*-disalicylidene-(*R,R*)-1,2-diphenyl-1,2-ethanediamine) in the solid state upon heating, on grinding, and by exposure to acetonitrile and chloroform vapor was reported.[4,5] Unfortunately, the

mechanism was not revealed because the crystal structure of the converted forms could not be determined. This paper reports preparation and crystal structures of [VO{3-Xsal-(*R,R*)-2,4-ptn}] (H$_2${3-Xsal-(*R,R*)-2,4-ptn}: *N,N′*-di-3-Xsalicylidene-(*R,R*)-2,4-pentanediamine; X = EtO(ethoxy), MeO (methoxy), and H) (Figure 1), which have a six-membered N−N chelate ring containing two methyl substituents. In the present case, conversion from a polymeric to a monomeric form was observed for the 3-ethoxy substituted complex, and crystal structures of both forms have been determined. The mechanism of the conversion between them is discussed in detail.

Experimental Section

Preparation of the Ligands. The ligands, H$_2${3-Xsal-(*R,R*)-2,4-ptn} (X = EtO, MeO, and H) were prepared by the reaction of (*R,R*)-2,4-pentanediamine[6] with 2 equiv amounts of 3-Xsalicylaldehyde (X = ethoxy, methoxy, and H) in ethanol. The reaction mixture was evaporated to yield an oily product, which was used for the following reaction without purification.

[VO{3-Xsal-(*R,R*)-2,4-ptn}]; Orange Polymeric Forms {1 (X = EtO), 3 (X = MeO), and 4 (X = H)} and a Green Monomeric Form {2 (X = EtO)}. To a methanol solution (15 mL) of the ligand (1 mmol) and pyridine (2 mL) was added a hot methanol solution (45 mL) of vanadyl sulfate (1 mmol, 0.25 g). The solution was refluxed for 15 min and allowed to stand at room temperature. For the 3-ethoxy substituted complex, a green powder of **2** was precipitated. It was collected by filtration and washed with methanol. Yield of **2**, 0.31 g (66%). Anal. Calcd for [VO{3-EtOsal-(*R,R*)-

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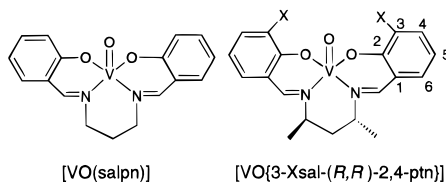
Figure 1. [VO(salpn)] and [VO{3-Xsal-(*R,R*)-2,4-ptn}] (X = EtO, MeO, and H).

2,4-ptn}] (C$_{23}$H$_{28}$N$_2$O$_5$V): C, 59.61; H, 6.09; N, 6.05%. Found: C,- 59.75; H, 6.20; N, 6.13%. IR (Nujol, cm^{-1}): 985[ν(V=O)]. UV− vis spectrum {DMSO, σ/10^3 cm^{-1} (log(ϵ/M^{-1} cm^{-1}))}: 13.0 (1.44), 18.6 (2.02), 26.3 (3.80), 34.7 (sh), 38.0 (4.38). For the 3-methoxy and nonsubstituted (X = H) complexes, the reaction mixture was evaporated to give an oily residue, which was suspended in ethanol to yield an orange crude product. It was collected by filtration and recrystallized from dichloromethane and ethanol. Yield of **3**, 0.26 g (59%). Anal. Calcd for [VO{3-MeOsal-(*R,R*)-2,4-ptn}]·0.5H$_2$O (C$_{21}$H$_{25}$N$_2$O$_{5.5}$V): C, 56.76; H, 5.67; N, 6.30%. Found: C, 56.99; H, 5.57; N, 6.34%. IR (Nujol, cm^{-1}): 876 [ν(V=O)], 3543, 3595 [ν-(O−H)]. UV−vis spectrum {DMSO, σ/10^3 cm^{-1} (log(ϵ/M^{-1}cm^{-1}))}: 12.9 (1.52), 18.7 (2.01), 26.4 (3.74), 37.8 (4.29). Yield of **4**, 0.23 g (61%). Anal. Calcd for [VO{sal-(*R,R*)-2,4-ptn}] (C$_{19}$H$_{20}$N$_2$O$_3$V): C, 60.80; H, 5.37; N, 7.47%. Found: C, 60.64; H, 5.47; N, 7.39%. IR (Nujol, cm^{-1}): 879 [ν(V=O)]. UV−vis spectrum {DMSO, σ/10^3 cm^{-1} (log(ϵ/M^{-1}cm^{-1}))}: 13.0 (1.54), 18.6 (2.13), 27.6 (3.98), 37.9 (4.39).

The green powder of **2** (0.140 g, 0.30 mmol) was suspended in water−acetonitrile (4:1 (v/v), 150 mL) and left for 4 days at room temperature with occasional stirring. The green powder of **2** gradually changed to the orange microcrystals of **1**. They were collected by filtration and dried. Yield of **1**: 0.124 g (85%). Anal. Calcd for [VO-{3-EtOsal-(*R,R*)-2,4-ptn}]·0.5H$_2$O (C$_{23}$H$_{29}$N$_2$O$_{5.5}$V): C, 58.47; H, 6.19; N, 5.93%. Found: C, 58.68; H, 6.03; N, 5.95%. IR (Nujol, cm^{-1}): 867 [ν(V=O)], 3552, 3601 [ν(O−H)].

Slow evaporation of acetonitrile solutions of orange **3** and **4** at 50 °C gave amorphous green products. IR spectra of these green products in Nujol mulls show ν(V=O) at 985 and 986 cm^{-1}, respectively. These amorphous green products were unstable and gradually turned back to orange crystalline **3** and **4**, respectively, on standing in the air.

Thermal Conversion of the Orange Crystals into the Green Ones in the Solid State. Orange crystals of **1** were completely converted into green ones of **2** upon heating at 170 °C for 10 min. The X-ray diffraction pattern of the heated product of **1** was identical with that of **2**. Orange crystals of **3** were also converted into green ones (IR data ν(V=O) = 985 cm^{-1}) upon heating at 200 °C. However, the reaction of **3** was accompanied by decomposition of the complex, and a pure green product could not be obtained.

Thermal Analysis. Thermal analyses were carried out using a ULVAC TA-1500 and a Perkin-Elmer DSC 7 thermal analyzer. Thermogravimetry (TG) and differential scanning calorimetry (DSC) of **1** up to 250 °C were carried out with the heating rates of 10 and 5 °C min^{-1}, respectively. TG measurement showed 2.5% weight loss between 52−67 °C, which corresponds to 0.66 molecule of water per vanadium complex. DSC measurement showed heat absorption (6.0 ± 0.4 kJ mol^{-1}) at 165 °C.

Crystal Structure Determination. Orange crystals **1** were grown from an acetonitrile solution together with a small amount of green **2**. Green crystals of **2** were grown by slow evaporation of a methanol− dichloromethane (1:1 (v/v)) solution. An orange needle crystal (0.08 × 0.12 × 1.00 mm) of **1** and a green prism crystal (0.40 × 0.45 × 0.70 mm) of **2** were used for the X-ray measurements. The diffraction data were collected on a Rigaku AFC-5 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) up to 2θ = 50° for **1** and 2θ = 55° for **2**. Intensity data were collected using ω scans for **1** and θ - 2θ scans for **2**. Three standard reflections were measured at every 100 reflections. Independent 2312 and 2979 reflections were measured for **1** and **2**, respectively. Absorption correction was made by the numerical integration method from crystal shape. The structures were solved by direct methods and refined using 1469 and 2445 observed reflections [|F_o| > 3σ(|F_o|)] for **1** and **2**, respectively. The

Table 1. Crystallographic Data for **1** and **2**

	1	2
chem formula	VO$_6$N$_2$C$_{23}$H$_{30}$	VO$_5$N$_2$C$_{23}$H$_{28}$
fw	481.4	463.4
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a, Å	13.764(4)	10.393(2)
b, Å	21.544(4)	22.278(2)
c, Å	7.682(5)	9.866(2)
V, Å^3	2278.0(17)	2289.0(7)
Z	4	4
ρ_{calc}, g/cm^3	1.404	1.345
μ, cm^{-1}	4.77	4.69
λ, Å	0.710 73	0.710 73
temp, °C	25	25
R^a	0.0643	0.0551
$R_w{}^b$	0.0535	0.0558

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$.

Table 2. Fractional Coodinates and Thermal Parameters for **1**

atom	x	y	z	U_{eq}/U_{iso},^{a} Å^2
V(1)	0.2589(1)	−0.0019(2)	0.3783(2)	0.0280(4)
O(2)	0.3673(7)	−0.0606(5)	0.404(1)	0.036(3)
O(3)	0.3568(7)	0.0632(5)	0.377(1)	0.033(3)
O(4)	0.2298(4)	−0.0063(6)	0.1748(6)	0.038(3)
O(5)	0.539(1)	−0.1164(7)	0.364(2)	0.088(6)
O(6)	0.518(1)	0.1256(6)	0.370(2)	0.065(5)
N(7)	0.1668(8)	−0.0727(5)	0.472(1)	0.026(3)
N(8)	0.1545(8)	0.0675(5)	0.424(1)	0.026(3)
C(9)	0.368(1)	−0.1192(9)	0.446(2)	0.043(6)
C(10)	0.457(1)	−0.1504(9)	0.440(2)	0.052(6)
C(11)	0.630(1)	−0.144(1)	0.357(3)	0.15(1)
C(12)	0.702(2)	−0.090(2)	0.310(5)	0.28(2)
C(13)	0.470(1)	−0.2084(9)	0.493(3)	0.069(7)
C(14)	0.388(2)	−0.241(1)	0.567(3)	0.10(1)
C(15)	0.301(2)	−0.212(1)	0.574(3)	0.10(1)
C(16)	0.290(1)	−0.1539(8)	0.519(3)	0.047(5)
C(17)	0.194(1)	−0.1261(6)	0.524(2)	0.037(5)
C(18)	0.057(1)	−0.0640(8)	0.479(2)	0.057(5)
C(19)	0.013(1)	−0.0870(7)	0.309(2)	0.072(6)
C(20)	0.0250(6)	0.002(1)	0.521(1)	0.045(3)
C(21)	0.0523(9)	0.0518(6)	0.397(2)	0.045(4)
C(22)	−0.0176(9)	0.1061(8)	0.395(2)	0.066(6)
C(23)	0.179(1)	0.1222(8)	0.484(2)	0.044(5)
C(24)	0.272(1)	0.1471(8)	0.508(2)	0.042(5)
C(25)	0.283(2)	0.2089(9)	0.580(3)	0.070(7)
C(26)	0.362(2)	0.244(1)	0.573(3)	0.10(1)
C(27)	0.440(2)	0.2167(9)	0.507(3)	0.065(7)
C(28)	0.442(2)	0.1564(9)	0.434(2)	0.062(7)
C(29)	0.609(2)	0.151(1)	0.371(3)	0.12(1)
C(30)	0.685(1)	0.115(1)	0.276(3)	0.12(1)
C(31)	0.358(1)	0.1185(7)	0.442(2)	0.045(6)
O(32)	0.570(1)	−0.011(2)	0.491(3)	0.38(1)

^{a} $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

calculations were performed using CRYSTAN-GM software[7] on a SUN SPARC10 workstation. Site occupancy of the water of crystallization of **1** {O(32)} was tentatively assumed to be unity, although the large thermal parameter and elemental and thermal analytical data suggest incomplete population. Large thermal vibration was also observed for the carbon atoms of the ethoxy substituents {C(11), C(12), C(29), and C(30)} in **1**, suggesting positional disorder. Non-hydrogen atoms were treated anisotropically except for O(32) of **1**. Hydrogen atoms attached to carbon atoms were introduced at ideal positions. The absolute structures were assigned on the basis of the known configuration of (*R,R*)-2,4-pentanediamine. The final R and R_w values were 0.0643 and 0.0535 for **1** and 0.0551 and 0.0558 for **2**. Refinement with the enantiometric structures gave R = 0.0647 and R_w = 0.0544 for **1** and R = 0.0606 and R_w = 0.0612 for **2**. Crystal data and experimental details are listed in Table 1 and atomic parameters in Tables 2 and 3.

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Table 3. Fractional Coordinates and Thermal Parameters for **2**

atom	x	y	z	U_{eq},[a] $Å^2$
V(1)	0.23042(5)	0.11559(2)	0.37639(6)	0.0370(1)
O(2)	0.4070(2)	0.0967(1)	0.3280(2)	0.046(1)
O(3)	0.2876(2)	0.1961(1)	0.3347(2)	0.044(1)
O(4)	0.1339(2)	0.0954(1)	0.2614(3)	0.053(1)
O(5)	0.6489(2)	0.0971(1)	0.2124(3)	0.057(1)
O(6)	0.3689(3)	0.2864(1)	0.1711(3)	0.069(1)
N(7)	0.2376(3)	0.0405(1)	0.5014(3)	0.045(1)
N(8)	0.1107(3)	0.1569(1)	0.5187(3)	0.044(1)
C(9)	0.4942(3)	0.0599(1)	0.3741(3)	0.038(1)
C(10)	0.6190(3)	0.0603(2)	0.3189(3)	0.043(1)
C(11)	0.6603(4)	0.1585(2)	0.2438(5)	0.080(2)
C(12)	0.7781(6)	0.1733(2)	0.3238(6)	0.096(2)
C(13)	0.7114(3)	0.0225(2)	0.3683(4)	0.052(1)
C(14)	0.6849(3)	−0.0182(2)	0.4723(4)	0.055(1)
C(15)	0.5654(3)	−0.0210(2)	0.5254(4)	0.050(1)
C(16)	0.4676(3)	0.0179(1)	0.4766(4)	0.041(1)
C(17)	0.3403(3)	0.0099(2)	0.5312(4)	0.046(1)
C(18)	0.1188(3)	0.0138(2)	0.5600(4)	0.056(1)
C(19)	0.0742(4)	−0.0384(2)	0.4760(6)	0.087(2)
C(20)	0.0123(3)	0.0607(2)	0.5769(4)	0.062(1)
C(21)	0.0525(3)	0.1214(2)	0.6309(4)	0.059(1)
C(22)	0.1428(4)	0.1199(2)	0.7522(4)	0.079(2)
C(23)	0.0678(3)	0.2108(2)	0.5056(4)	0.046(1)
C(24)	0.1090(3)	0.2544(2)	0.4080(3)	0.044(1)
C(25)	0.0408(4)	0.3094(2)	0.4015(4)	0.059(1)
C(26)	0.0828(4)	0.3541(2)	0.3179(5)	0.073(2)
C(27)	0.1913(4)	0.3459(2)	0.2389(4)	0.064(1)
C(28)	0.2590(3)	0.2929(2)	0.2431(3)	0.049(1)
C(29)	0.3725(6)	0.2526(5)	0.0645(7)	0.226(6)
C(30)	0.4782(7)	0.2621(4)	−0.0264(6)	0.171(4)
C(31)	0.2189(3)	0.2456(1)	0.3283(3)	0.041(1)

[a] $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Other Measurements. IR spectra were recorded on a JASCO A-202 spectrophotometer by a Nujol mull method. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. X-ray powder diffraction (XRD) patterns were measured on a Rigaku RAD-C diffractometer with monochromatized Cu Kα radiation.

Results and Discussion

Synthesis. A new series of oxovanadium(IV) complexes with tetradentate Schiff base ligands derived from (*R*,*R*)-2,4-pentanediamine was prepared. Reactions of the Schiff base ligands with vanadyl sulfate in methanol gave a green powder of **2** (3-ethoxy complex) and orange powders of **3** (3-methoxy complex) and **4** (nonsubstituted complex) in moderate yields. Orange microcrystals of **1** (3-ethoxy complex) were prepared by suspending **2** in water−acetonitrile (4:1 (v/v)) and standing for 4 days at room temperature with occasional stirring. IR spectra of these complexes show ν(V=O) in the region 867−879 cm^{-1} for **1**, **3**, and **4** and at 985 cm^{-1} for **2**. Tetradentate Schiff base−oxovanadium(IV) complexes generally show ν(V=O) around 850 cm^{-1} for a polymeric form and around 970 cm^{-1} for a monomeric form.[1,4] Thus, orange **1**, **3**, and **4** are assigned to polymeric structures, and green **2** is assigned to a monomeric structure. Green **2** is the first example of monomeric crystal of the Schiff base−oxovanadium(IV) complex which has a six-membered N−N chelate ring. Introduction of bulky substituents at the 3-positions of the salicylaldehyde moieties of the complex seems to facilitate the formation of a monomeric crystal structure. The IR spectra of **1** and **3** show two sharp ν(O−H) bands in the region 3543−3601 cm^{-1}. These two bands are assigned to the O−H stretching frequency of a water molecule, which is detected by X-ray analysis for **1**. Electronic spectra of the complexes in this study show d−d bands around 13 000 and 18 700 cm^{-1} and CT bands around 27 000 and 38 000 cm^{-1} in DMSO solution, which are similar to those in the spectra of [VO(salpn)] in polar solvents.[8]
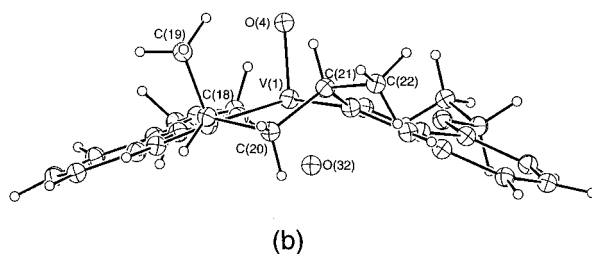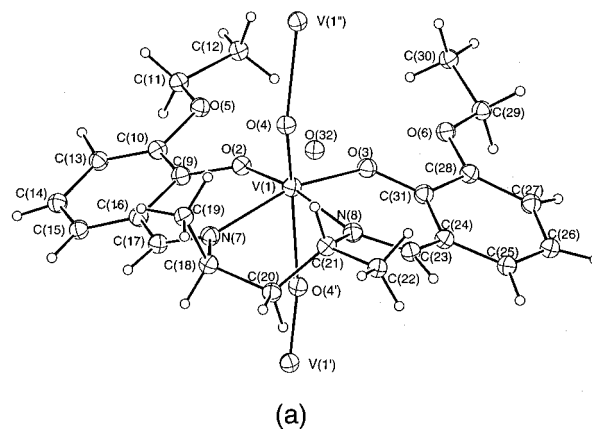

Figure 2. (a) Perspective view and (b) side view of **1**. Non-hydrogen atoms and hydrogen atoms are represented by circles of radius 0.2 and 0.1 Å, respectively. The ORTEP drawing with 20% probability ellipsoids is deposited as Supporting Information.
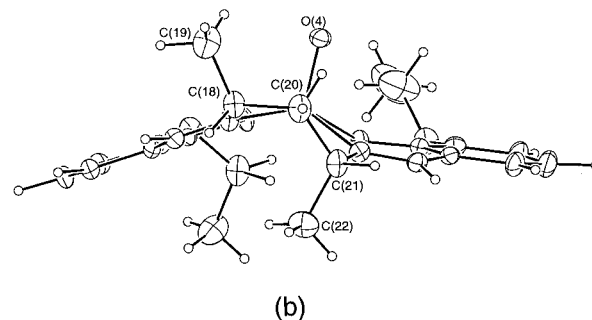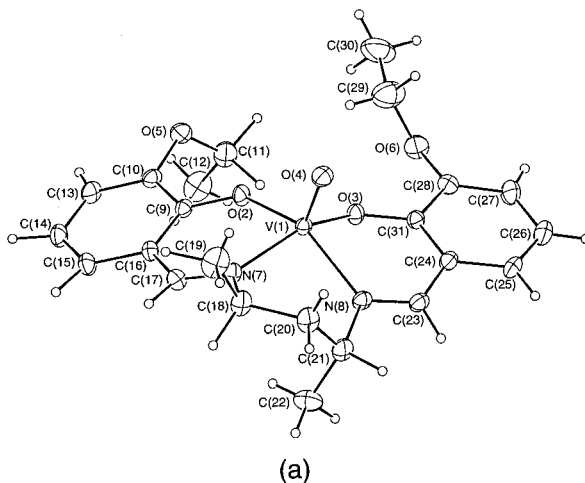
Figure 3. (a) Perspective view and (b) side view of **2** with 20% probability ellipsoids.

Evaporation of acetonitrile solutions of **3** and **4** gave amorphous green products, which gradually turned back to orange crystalline **3** and **4**, respectively, on standing in air. The
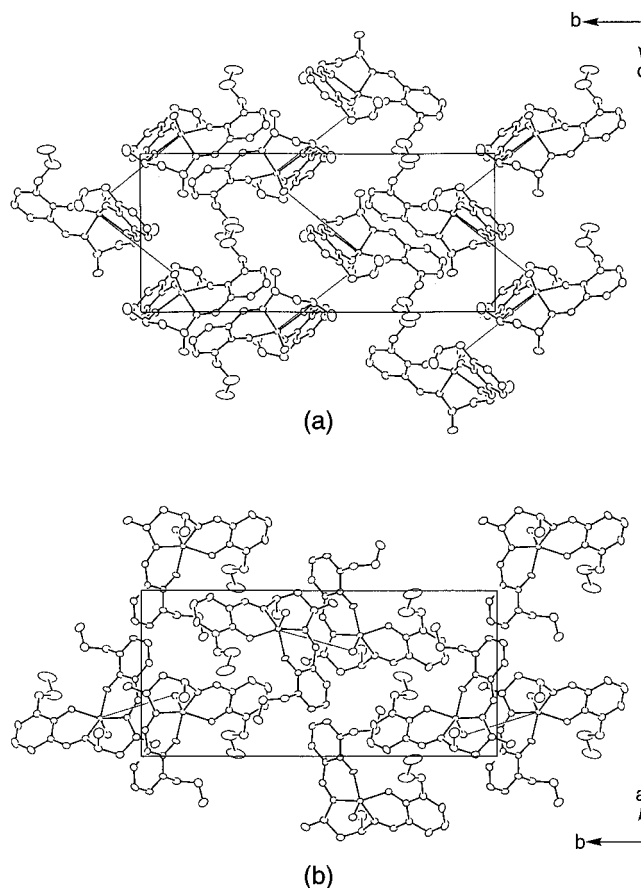
(a)

(b)
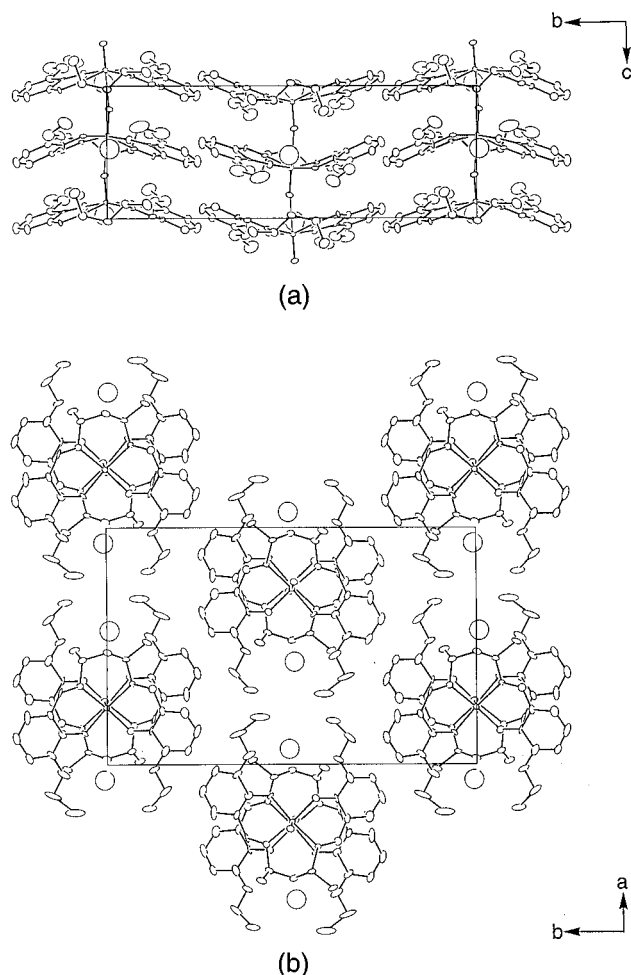
Figure 4. Projections of the crystal structure of **1** along (a) *a*- and (b) *c*-axes. Vanadium atoms and terminal oxygen atoms of the neighboring complexes are connected with solid lines to show the arrangements of the molecules.

IR data of these amorphous products show ν(V=O) at 985 and 986 cm^{-1}, indicating monomeric structures. Further investigation of these products was not carried out.

X-ray Crystal Structures of Polymeric (1) and Monomeric (2) Forms of [VO{3-EtOsal-(*R,R*)-2,4-ptn}]. X-ray structure analyses of **1** and **2** were carried out. The space group of **1** and **2** is identical (*P*2$_1$2$_1$2$_1$), and unit cell parameters are related (Table 1). Molecular structures of **1** and **2** are shown in Figures 2 and 3, and crystal structures, in Figures 4 and 5. The molecular structure of **1** is represented by spheres in Figure 2 because of large thermal vibration of the ethoxy substituents and water. Selected bond lengths and angles are listed in Table 4. Crystal **1** has water of crystallization (O(32)), and the complex takes a polynuclear linear-chain structure. The individual complexes take a distorted-octahedral coordination with a terminal oxygen atom of the adjacent molecule (O(4′)) at the sixth position. The V(1)···O(4′) distance is 2.290(6) Å, which is a little longer than that of [VO(salpn)] (2.213(9) Å).[1] Crystal **2** has no water of crystallization, and the complex takes a monomeric structure with square-pyramidal coordination geometry. The V(1)=O(4) distances in **1** and **2** are 1.617(6) and 1.582(3) Å, respectively. The displacement of V(1) from the N(7)N(8)O(2)O(3) coordination plane toward O(4) is 0.32(1) Å for **1** and 0.560(4) Å for **2**.

A striking difference between **1** and **2** is observed in the conformation of the six-membered N−N chelate ring and the

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(a)

(b)

Figure 5. Projections of the crystal structure of **2** along (a) *a*- and (b) *c*-axes. Vanadium atoms and terminal oxygen atoms of the neighboring complexes are connected with solid lines to show the arrangements of the molecules.

Table 4. Selected Bond Lengths (*l*/Å) and Bond Angles (*ϕ*/deg) of **1** and **2**[a]

	1	**2**
V(1)−O(2)	1.965(11)	1.943(3)
V(1)−O(3)	1.945(11)	1.935(3)
V(1)−O(4)	1.617(6)	1.582(3)
V(1)−N(7)	2.110(12)	2.081(3)
V(1)−N(8)	2.102(12)	2.091(3)
V(1)−O(4′)	2.290(6)	
O(2)−V(1)−O(3)	86.5(5)	81.8(1)
O(2)−V(1)−O(4)	104.5(5)	111.1(2)
O(2)−V(1)−N(7)	87.5(5)	86.5(2)
O(2)−V(1)−N(8)	163.6(5)	145.4(2)
O(3)−V(1)−O(4)	102.0(5)	107.8(2)
O(3)−V(1)−N(7)	160.0(4)	149.4(2)
O(3)−V(1)−N(8)	87.8(5)	85.3(1)
O(4)−V(1)−N(7)	98.0(5)	102.7(2)
O(4)−V(1)−N(8)	91.8(5)	103.4(2)
N(7)−V(1)−N(8)	92.7(5)	88.6(2)
V(1)···O(4′)−V(1′)	160.2(5)	
O(4′)···V(1)−O(4)	169.5(3)	

[a] Primed atoms are generated by 1/2 − *x*, −*y*, 1/2 + *z*.

orientation of the ethoxy substituents. The six-membered N−N chelate ring of **1** takes a chair form with one of the methyl groups (C(19)) in the axial position on the same side of the oxo atom (O(4)) and the other methyl (C(22)) in the equatorial position (Figure 2). On the other hand, in **2** it takes a distorted flattened boat form with one of the methyls (C(22)) in the axial position opposite to the oxo atom and the other methyl (C(19)) in the intermediate position between equatorial and axial (Figure 3). The water molecule of **1** is hydrogen bonded with four oxygen atoms of the ligand. The distances O(2)···O(32),

O(3)···O(32), O(5)···O(32), and O(6)···O(32) are in the range of 2.52(5)−3.45(3) Å. Both of the two ethoxy substituents are oriented in the equatorial position to form the hydrogen bond. The folding of water of crystallization by two ethoxy groups is also observed in [VO(3-EtO(salen))] (H$_2$(3-EtO(salen)): *N,N'*-di-3-ethoxysalicylideneethylenediamine).[9] There is no water of crystallization in **2**, and ethoxy substituents are oriented in the axial positions opposite to each other. The steric effects of these axially-oriented methyl and ethoxy substituents seem to prevent the V=O···V=O··· linkage and lead to formation of a monomeric crystal structure for [VO{3-EtOsal-(*R,R*)-2,4-ptn}], although Schiff base−oxovanadium(IV) complexes having a six-membered N−N chelate ring usually take a linear chain structure.

Thermal Conversion from a Polymeric to a Monomeric Structure in the Solid State. Orange polymeric crystals of **1** were converted into green monomeric crystals of **2** in the solid state upon heating at 170 °C for 10 min. Green crystals of **2** were converted into orange crystals of **1** by being suspended in water−acetonitrile (4:1 (v/v)) for 4 days. The thermal conversion from **1** to **2** proceeded slowly, with a change of color and cracking of the crystals. Characterization of the crystal structures before and after the thermal conversion was based on the IR spectra and X-ray powder diffraction. No intermediate state of the reaction was observed during the conversion. Orange crystals of **3** were also converted into green monomeric ones (ν(V=O) = 985 cm^{-1}) upon heating at 200 °C, but the reaction was accompanied by decomposition of the complex. No structural change occurred for **4** upon heating except for decomposition. Thermogravimetric measurement of **1** showed loss of water of crystallization between 52 and 67 °C. An endothermic anomaly (6.0 ± 0.4 kJ mol^{-1}) assignable to the conversion was observed at 165 °C by DSC with the heating rate 5 °C min^{-1}.

The X-ray studies of **1** and **2** indicate that the structural changes during the heat conversion involve three processes: (1) loss of water of crystallization and orientational change of the ethoxy substituents; (2) rearrangement of oxovanadium(IV) complexes from a polymeric linear chain to a monomeric crystal structure; (3) conformational change of the six-membered N−N chelate ring from a chair form to a flattened boat form. Thermogravimetric data indicates that the rearrangement of the complexes occurs after the loss of crystal water, which is removed below 100 °C. Figures 4 and 5 show the packing diagrams of **1** and **2** viewed along the *a* and *c* axes. In **1** the linear V=O···V=O··· chains run along the 2$_1$ screw axes parallel to the *c* axis. The six-membered N−N chelate rings in polymeric chains are arranged up and down alternately in the *a* direction. After the loss of water of crystallization, the complexes seem to slide along the +*b* and −*b* direction alternately with a little rotation, and the V=O···V=O linkage will be broken upon heating to yield the monomeric structure of **2**. The conformation of the six-membered N−N chelate ring will be converted from a chair to a boat form during the structural transformation.

Supporting Information Available: An ORTEP drawing of **1** (1 page). One X-ray crystallographic file, in CIF format, is available. Access and ordering information is given on any current masthead page.

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