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Thermal Dehydrogenation of Oxovanadium(IV) Complexes with Schiff Base Ligands Derived from *meso*-1,2-Diphenyl-1,2-ethanediamine in the Solid State

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Introduction

Tetradentate Schiff base−oxovanadium(IV) complexes take green monomeric structures with square-pyramidal coordination or orange linear chain structures (V═O···V═O···) with distorted octahedral coordination[1] in the solid state. The complexes are used as catalysts for oxidation reactions[2,3] and as core groups of liquid crystalline polymers.[4] Their reactivities and structural characteristics attract the interest of many researchers. Recently, we reported thermal reactions of Schiff base−oxovanadium(IV) complexes in the solid state, which include isomerization of diastereomeric pairs of the complex[5] and interconversion between monomeric and polymeric forms of the complexes.[6,7] These studies suggest the migration of terminal oxygen (V═O) atoms to the adjacent molecules[5] or the rearrangement of molecules[6,7] upon heating. In the course of these investigations, it was found that, upon being heated at 210 °C in the solid state, the [VO(Xsal-*meso*-stien)] (H_2(Xsal-*meso*-stien) = *N,N′*-di-Xsalicylidene-(*R,S*)(*S,R*)-1,2-diphenyl-1,2-ethanediamine; X = 3-EtO (ethoxy), 5-MeO (methoxy), 5-Br) complexes were transformed into [VO(Xsalton)] (H_2(Xsalton) = *N,N′*-di-Xsalicylidene-1,2-diphenyl-1,2-ethenediamine), which have a C═C double bond in the five-membered chelate ring moiety (Figure 1). This paper reports synthesis and characterization of [VO(Xsal-*meso*-stien)] and the thermal reaction of the complexes in the solid state.

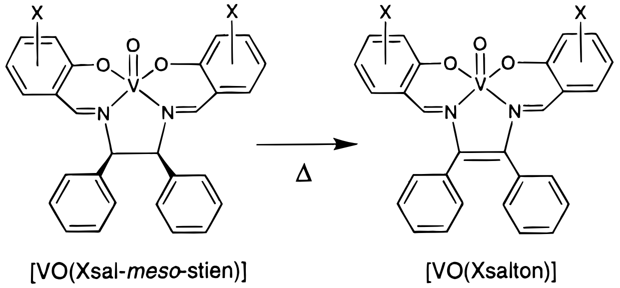

Figure 1. Thermal transformation of [VO(Xsal-*meso*-stien)] (X = 3-EtO, 5-MeO, 5-Br) to [VO(Xsalton)] in the solid state.

Experimental Section

Preparation of the Ligands. The ligands H_2(Xsal-*meso*-stien) (X = 3-EtO, 4-MeO, 5-MeO, 5-Br, 5-NO_2, H) were quantitatively prepared by the reaction of *meso*-1,2-diphenyl-1,2-ethanediamine[8] with 2 equiv amounts of X-salicylaldehyde in ethanol. The yellow precipitate of the ligand was collected by filtration and dried.

[VO(Xsal-*meso*-stien)] (X = 3-EtO, 4-MeO, 5-MeO, 5-Br, 5-NO_2, H). To a hot methanol solution (50 mL) of vanadyl sulfate (0.25 g, 1 mmol) was added the ligand H_2(Xsal-*meso*-stien) (1 mmol) and pyridine (2 mL), and the mixture was stirred for 1 h at 60 °C. The resulting green (X = 3-EtO, 4-MeO, 5-MeO, 5-Br, H) or orange (X = 5-NO_2) precipitate was collected by filtration and washed with ether. Yield of [VO(3-EtOsal-*meso*-stien)]: 0.41 g (71%). Anal. Calcd for $C_{32}H_{30}N_2O_5V$: C, 67.01; H, 5.27; N, 4.89. Found: C, 66.90; H, 5.12; N, 4.88. IR (KBr, cm^{-1}): 978 [ν(V═O)], 1593 [ν(C═N)]. UV−vis spectrum $\{CH_3CN, \sigma/10^3\ cm^{-1}\ (\log(\epsilon/M^{-1}\ cm^{-1}))\}$: 14.7 (sh), 16.7 (2.13), 25.7 (3.85), 33.4 (4.36), 42.5 (4.62). Yield of [VO(4-MeOsal-*meso*-stien)]: 0.47 g (86%). Anal. Calcd for $C_{30}H_{26}N_2O_5V$: C, 66.06; H, 4.80; N, 5.14. Found: C, 66.13; H, 4.79; N, 4.99. IR (KBr, cm^{-1}): 985 [ν(V═O)], 1592 [ν(C═N)]. UV−vis spectrum $\{CH_3CN, \sigma/10^3\ cm^{-1}\ (\log(\epsilon/M^{-1}\ cm^{-1}))\}$: 15.0 (sh), 16.8 (2.23), 21.1 (sh), 25.4 (sh), 28.2 (4.25), 32.8 (4.44), 39.9 (4.60). Yield of [VO(5-Brsal-*meso*-stien)]: 0.56 g (87%). Anal. Calcd for $C_{28}H_{20}N_2Br_2O_3V$: C, 52.28; H, 3.13; N, 4.36. Found: C, 52.56; H, 3.05; N, 4.64. IR (KBr, cm^{-1}): 984 [ν(V═O)], 1612 [ν(C═N)]. The UV−vis spectral data of [VO(5-Brsal-*meso*-stien)] could not be obtained because of the low solubility of the complex. Yield of [VO(5-NO_2sal-*meso*-stien)]: 0.49 g (85%). Anal. Calcd for $C_{28}H_{20}N_4O_7V$: C, 58.44; H, 3.50; N, 9.74. Found: C, 58.17; H, 3.43; N, 9.97. IR (KBr, cm^{-1}): 903 [ν(V═O)], 1604 [ν(C═N)]. UV−vis spectrum $\{DMSO, \sigma/10^3\ cm^{-1}\ (\log(\epsilon/M^{-1}\ cm^{-1}))\}$: 13.3 (1.91), 17.4 (sh), 20.9 (sh), 27.3 (4.56), 34.8 (sh), 38.1 (4.55). For the 5-MeO and nonsubstituted (X = H) complexes, a mixture of two isomers (ca. 5:1) was obtained. The ratio of the isomers was estimated by high-performance liquid chromatography (HPLC). One of the isomers, which is a main product and has a lower solubility than the other one, was isolated from the mixture by recrystallization from acetonitrile and ether. Yield of [VO(5-MeOsal-*meso*-stien)]: 0.21 g (39%). Anal. Calcd for $C_{30}H_{26}N_2O_5V$: C, 66.06; H, 4.80; N, 5.14. Found: C, 65.82; H, 4.81; N, 5.26. IR (KBr, cm^{-1}): 978 [ν(V═O)], 1601 [ν(C═N)]. UV−vis spectrum $\{CH_3CN, \sigma/10^3\ cm^{-1}\ (\log(\epsilon/M^{-1}\ cm^{-1}))\}$: 15.0 (sh), 16.6 (2.31), 24.8 (4.14), 34.9 (sh), 40.0 (4.78). Yield of [VO(sal-*meso*-stien)]: 0.13 g (27%). Anal. Calcd for $C_{28}H_{22}N_2O_3V$: C, 69.28; H, 4.57; N, 5.77. Found: C, 68.99; H, 4.41; N, 5.86. IR (KBr, cm^{-1}): 987 [ν(V═O)], 1604 [ν(C═N)]. UV−vis spectrum

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{CH_3CN, $\sigma/10^3$ cm^{-1} (log(ϵ/M^{-1} cm^{-1}))}: 14.5 (sh), 17.1 (1.98), 20.6 (sh), 27.2 (3.82), 35.4 (4.12), 41.4 (4.44).

Synthesis of [VO(Xsalton)] (X = 3-EtO, 5-MeO, 5-Br) upon Heating [VO(Xsal-*meso*-stien)] in the Solid State. The green powder of [VO(Xsal-*meso*-stien)] (X = 3-EtO, 5-MeO, 5-Br) (0.2 mmol) was heated at 210 °C for 3 h (X = 5-MeO), 5 h (X = 3-EtO), and 15 h (X = 5-Br) in the air. The brown reaction product was dissolved in dichloromethane, and the undissolved V(V) byproduct was removed by filtration. The filtrate was evaporated to dryness, and the residue was recrystallized from acetonitrile. Yield of [VO(3-EtOsalton)-(H_2O)]·$0.5CH_3CN$·$0.5H_2O$: 0.056 g (45%). Anal. Calcd for $C_{33}H_{32.5}N_{2.5}O_{6.5}V$: C, 64.02; H, 5.29; N, 5.66. Found: C, 63.93; H, 5.00; N, 5.36. IR (Nujol, cm^{-1}): 973 [ν(V=O)], 1584 [ν(C=N)], 3436 [ν(O−H)]. UV−vis spectrum {CH_3CN, $\sigma/10^3$ cm^{-1} (log(ϵ/M^{-1} cm^{-1}))}: 15.2 (sh), 23.0 (4.01), 27.0 (4.40), 32.3 (4.29), 40.2 (sh). Yield of [VO(5-MeOsalton)]: 0.067 g (62%). Anal. Calcd for $C_{30}H_{24}N_2O_5V$: C, 66.30; H, 4.45; N, 5.15. Found: C, 66.01; H, 4.25; N, 5.32. IR (KBr, cm^{-1}): 989 [ν(V=O)], 1583 [ν(C=N)]. UV−vis spectrum {CH_3CN, $\sigma/10^3$ cm^{-1}(log(ϵ/M^{-1} cm^{-1}))}: 15.2 (sh), 19.6 (sh), 22.3 (3.97), 27.4 (4.17), 33.9 (sh), 40.2 (4.60). Yield of [VO(5-Brsalton)]: 0.053 g (41%). Anal. Calcd for $C_{28}H_{18}N_2O_3V$: C, 52.45; H, 2.83; N, 4.37. Found: C, 52.58; H, 3.15; N, 4.45. IR (KBr, cm^{-1}): 993 [ν(V=O)], 1597 [ν(C=N)]. UV−vis spectrum {CH_3CN, $\sigma/10^3$ cm^{-1} (log(ϵ/M^{-1} cm^{-1}))}: 14.2 (sh), 21.0 (4.08), 23.5 (4.11), 28.8 (4.31), 35.0 (sh), 37.8 (4.60).

Thermal Analysis. Thermogravimetry (TG) and differential scanning calorimetry (DSC) of [VO(3-EtOsal-*meso*-stien)]·H_2O were carried out using an ULVAC TA-1500 and a Perkin-Elmer DSC 7, respectively, in the temperature range 30−230 °C. The heating rate employed for TG was 2 °C min^{-1}, while for DSC it was 5 °C min^{-1}.

Crystal Structure Determination. Green crystals of [VO(3-EtOsal-*meso*-stien)]·H_2O (**1**) were grown from an acetone solution. Red crystals of [VO(3-EtOsalton)(H_2O)]·$0.5CH_3CN$·$0.5H_2O$ (**2**) were grown from an acetonitrile solution. A green prism crystal (0.70 × 0.20 × 0.20 mm) of **1** and a red platelike crystal (0.90 × 0.30 × 0.01 mm) of **2** were used for the X-ray measurements. The diffraction data were collected on a Rigaku AFC-5 four-circle diffractometer for **1** and on a Rigaku RAXIS-IICS IP camera for **2** with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Intensity data were collected using $\theta-2\theta$ scans up to $2\theta = 53°$ for **1** and $2\theta_{max} = 56°$ for **2** (data completeness: 87.7%): independent 6664 and 13 569 reflections were measured for **1** and **2**, respectively. Absorption correction was made by a numerical integration method from the crystal shape for **1**. The structures were solved by direct methods and refined using 4026 observed reflections [$|F_o| > 3\sigma(|F_o|)$] for **1** and 10 999 reflections [$|F_o|^2 > 2\sigma(|F_o|^2)$] for **2**, respectively. The calculations were performed using CRYSTAN-GM software[9] for **1** and using SIR-92[10] for direct methods and SHELXL-93[11] for full-matrix least-squares for **2**. All non-hydrogen atoms were treated anisotropically, and all hydrogen atoms attached to carbon atoms were introduced at ideal positions. Crystal data and experimental details are listed in Table 1.

Other Measurements. Cyclic voltammetric measurements were carried out on DMSO solutions (1 mM complex, 0.1 M $N(C_4H_9)_4BF_4$). A glassy carbon electrode, a Ag/$AgNO_3$ electrode (Ag/0.01 M $AgNO_3$), and a platinum wire were employed as the working, reference, and auxiliary electrodes, respectively. IR spectra were recorded on a JASCO A-202 spectrophotometer by a KBr or a Nujol mull method. UV−vis spectra were recorded on a JASCO V-570 spectrophotometer. HPLC was carried out with a Shimadzu LC-10AD pumping unit and a Shimpack CLC-ODS column (eluent: CH_3CN-H_2O (7:3 v/v)). The components of the chromatography were detected with a Shimadzu SPD-10A UV−vis detector at 250 nm.

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

	[VO(3-EtOsal-*meso*-stien)]·H_2O (**1**)	[VO(3-EtOsalton)(H_2O)]·$0.5H_2O$·$0.5CH_3CN$ (**2**)
empirical formula	$C_{32}H_{32}N_2O_6V$	$C_{33}H_{32.5}N_{2.5}O_{6.5}V$
fw	591.56	619.08
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	16.528(2)	19.884(1)
b, Å	11.031(2)	12.084(1)
c, Å	17.189(2)	26.192(2)
β, deg	112.482(8)	96.89(1)
V, Å^3	2895.8(7)	6247.9(8)
Z	4	8
ρ_{calcd}, g/cm^3	1.357	1.316
μ, cm^{-1}	3.90	3.66
λ, Å	0.710 73	0.710 73
temp, °C	25	25
R[a]	0.0606	0.0702
R_w[b]	0.0485	0.1556

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ for **1**, and $R = \sum|F_o^2 - F_c^2|/\sum F_o^2$ for **2**. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ and $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ for **1**. $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ and $w^{-1} = \sigma^2(F_o^2) + (0.0951P)^2 + 0.0000P$, where $P = (F_o^2 + 2F_c^2)/3$ for **2**.

Results and Discussion

Synthesis. A series of oxovanadium(IV) complexes with Schiff base ligands derived from *meso*-1,2-diphenyl-1,2-ethanediamine was prepared by the reaction of the Schiff base ligand with vanadyl sulfate in methanol containing pyridine. For [VO(Xsal-*meso*-stien)], there are two possible geometrical isomers arising from disposition of the terminal oxygen atom (V=O). One of the isomers was obtained for each X-substituted complex by the reaction.[12] The structure of the isomer was determined by an X-ray crystal structure analysis of [VO(3-EtOsal-*meso*-stien)] (vide infra).

IR spectra of the complexes show ν(V=O) in the region 978−987 cm^{-1} for the green 3-EtO, 4-MeO, 5-MeO, 5-Br, and nonsubstituted complexes and at 904 cm^{-1} for the orange 5-NO_2 substituted complex. Tetradentate Schiff base−oxovanadium(IV) complexes generally show ν(V=O) around 970 cm^{-1} for a monomeric form and around 860 cm^{-1} for a linear chain polymeric form.[1] Thus, the 3-EtO, 4-MeO, 5-MeO, 5-Br, and nonsubstituted complexes are assigned to monomeric structures. The orange 5-NO_2 substituted complex is assigned to a polymeric structure, although the ν(V=O) value of the complex is larger than those of other polymeric complexes.[13] The redox potentials for the V(V)/V(IV) couples determined by cyclic voltammetric measurements of the complexes in dimethyl sulfoxide show a systematic variation in the $E^{\circ\prime}$ values depending upon the nature of the substituents (X) of [VO(Xsal-*meso*-stien)] (Table 2). The $E^{\circ\prime}$ values are shifted to less positive potentials when electron-donating groups are introduced into the 5- or 3-position (X = 5-MeO, 3-EtO) and to more positive potentials when electron-withdrawing groups are introduced into the 5-position (X = 5-NO_2).

The brown [VO(Xsalton)] (X = 3-EtO, 5-MeO, 5-Br) complexes were prepared by heating the green powder of [VO(Xsal-*meso*-stien)] for 3 h (X = 5-MeO), 5 h (X = 3-EtO), and 15 h (X = 5-Br) at 210 °C in the air. The reaction product

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(12) Preparation of the other isomer and isomerization reaction of the complexes in the solid state will be reported in a separate paper.

(13) Orange needle crystals of [VO(5-NO_2sal-*meso*-stien)] were grown by vapor diffusion of methanol and ether into a DMSO solution of the complex. Crystal data: [VO(5-NO_2sal-*meso*-stien)]·CH_3OH, $C_{29}H_{24}N_4O_8V$, monoclinic $C2/c$, a = 31.017(2) Å, b = 7.906(3) Å, c = 27.077(2) Å, β = 123.087(3)°, V = 5563(2) Å^3, Z = 8, R = 0.105 for 2582 reflections. The complexes take a weak linear chain structure (V=O distance 1.59(1) Å, V···O distance 2.43(1) Å).

Table 2. Redox Potentials for the V(V)/V(IV) Couples vs Ag/Ag^{+} [a]

complex	$E^{\circ\prime}$/V (ΔE_p/mV)[b]
[VO(3-EtOsal-*meso*-stien)]	0.095(80)
[VO(4-MeOsal-*meso*-stien)]	0.209(74)
[VO(5-MeOsal-*meso*-stien)]	0.066(79)
[VO(5-Brsal-*meso*-stien)]	0.221(72)
[VO(5-NO_2sal-*meso*-stien)]	0.428(75)
[VO(sal-*meso*-stien)]	0.129(77)
[VO(3-EtOsalton)]	0.176(81)
[VO(5-MeOsalton)]	0.150(71)
[VO(5-Brsalton)]	0.293(75)

[a] Cyclic voltammograms were measured in dimethyl sulfoxide with Bu_4NBF_4 as a supporting electrolyte; scan rate is 0.1 V s^{-1}. Data for 1 mM ferrocenium/ferrocene: $E^{\circ\prime} = 0.172$ V. [b] $E^{\circ\prime}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials: $\Delta E_p = E_{pa} - E_{pc}$.

was recrystallized from dichloromethane to remove the V(V) byproduct, which is slightly soluble in dichloromethane. When [VO(sal-*meso*-stien)] was heated at 210 °C, formation of [VO(salton)] was observed. However, the pure [VO(salton)] could not be obtained because of low yield and difficulty in purification of the complex. Heating of [VO(4-MeOsal-*meso*-stien)] yielded only unknown V(V) product. No reaction occurred for [VO(5-NO_2sal-*meso*-stien)] upon heating at 210 °C. The IR spectra of the [VO(Xsalton)] complexes show ν(V=O) in the region 973−993 cm^{-1}, which indicated monomeric structures of the complexes. A ν(C=C) band of the 1,2-diphenyl-1,2-ethenediamine moiety cannot be assigned because the band is hidden by a strong ν(C=N) band around 1600 cm^{-1}. The electronic spectra show that the charge transfer bands of [VO(Xsalton)] (X = 3-EtO, 5-MeO, 5-Br) are shifted to lower energy than those of [VO(Xsal-*meso*-stien)]. The electronic spectra of [VO(Xsal-*meso*-stien)] show d−d bands around 15 000 and 17 000 cm^{-1} in acetonitrile. However, the d−d band around 17 000 cm^{-1} is hidden by a charge transfer band around 22 000 cm^{-1} for [VO(Xsalton)].[14] The redox potentials for the V(V)/V(IV) couples show that [VO(Xsalton)] (X = 3-EtO, 5-MeO, 5-Br) are more difficult to oxidize to V(V) than [VO(Xsal-*meso*-stien)].

Description of the Structures of [VO(3-EtOsal-*meso*-stien)]·H_2O (1) and [VO(3-EtOsalton)(H_2O)]·0.5CH_3CN·0.5H_2O (2). The molecular structures of **1** and **2** determined by X-ray structure analyses are shown in Figures 2 and 3. Crystal **1** includes water of crystallization (O(41)), and the geometry around the vanadium atom is a distorted square pyramid with the oxo atom (O(2)) at the apical position. The V(1)=O(2) distance is 1.597(3) Å, and the V(1) atom is displaced 0.585(5) Å toward the apical oxo ligand from the N(7)N(8)O(3)O(4) coordination plane. The five-membered N−N chelate ring takes a distorted gauche conformation with two phenyl groups located on the same side of the oxo ligand. The water molecule (O(41)) is hydrogen-bonded with four oxygen atoms of the ligand (O(3), O(4), O(5), O(6)) in the O···O range 2.979(4)−3.061(4) Å. Both of the two ethoxy substituents are oriented in the equatorial position to form the hydrogen bonds, which is observed in other 3-ethoxy substituted Schiff base−oxovanadium(IV) complexes.[7,15]

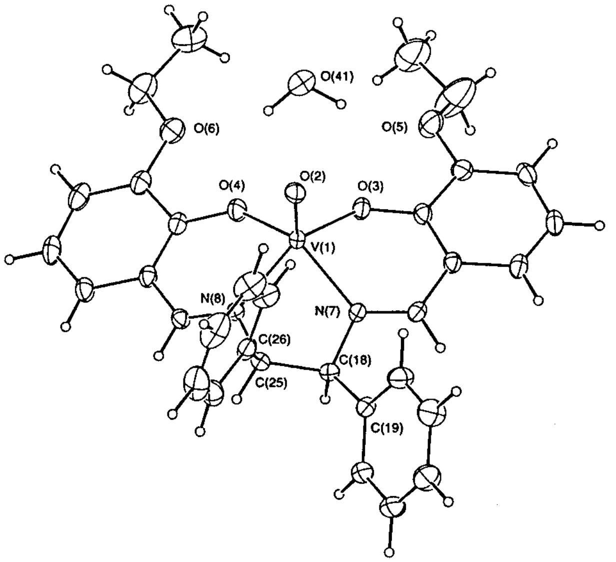

Figure 2. ORTEP drawing of **1** with 20% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): V(1)−O(2), 1.597(3); V(1)−O(3), 1.934(2); V(1)−O(4), 1.925(3); V(1)−N(7), 2.072(3), V(1)−N(8), 2.065(3); N(7)−C(18), 1.490(4); N(8)−C(25), 1.487(4); C(18)−C(25), 1.547(5); N(7)−V(1)−N(8), 77.9(1); N(7)−C(18)−C(19), 115.9(3); N(7)−C(18)−C(25), 109.8(3); C(19)−C(18)−C(25), 112.5(3); N(8)−C(25)−C(18), 106.9(3), N(8)−C(25)−C(26), 111.8(3); C(18)−C(25)−C(26), 117.3(3).

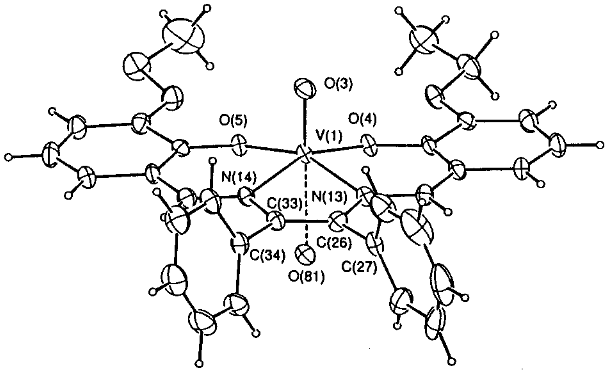

Figure 3. ORTEP drawing of **2** with 20% probability ellipsoids. One of the two independent molecules is shown. Selected bond lengths (Å) and bond angles (deg): V(1)−O(3), 1.584(3); V(1)−O(4), 1.962(3); V(1)−O(5), 1.948(3); V(1)−N(13), 2.056(3), V(1)−N(14), 2.059(3); V(1)−O(81), 2.406(3); N(13)−C(26), 1.408(5); N(14)−C(33), 1.415(5); C(26)−C(33), 1.353(6); N(13)−V(1)−N(14), 79.0(1); N(13)−C(26)−C(27), 121.4(4); N(13)−C(26)−C(33), 116.7(4); C(27)−C(26)−C(33), 121.8(4); N(14)−C(33)−C(26), 116.6(4), N(14)−C(33)−C(34), 120.1(4); C(26)−C(33)−C(34), 123.3(4).

In crystal **2**, the two independent molecules in the unit cell have an almost identical structure. The geometry around the vanadium atom is a distorted octahedron with a weak coordination of a water molecule (V(1)···O(81) distance: 2.406(3) Å) trans to the oxo ligand. The V(1) atom is displaced 0.339(3) Å from the equatorial N_2O_2 coordination plane. The five-membered chelate ring is almost flat with two phenyl groups oriented in the equatorial positions. The C(26)−C(33) bond distance (1.353(6) Å) and the bond angles around C(26) and C(33) (116.6(4)−123.3(4)°) indicate a C=C double bond in the five-membered chelate ring moiety.

Dehydrogenation Reaction. The green powder of [VO(Xsal-*meso*-stien)] (X = 3-EtO, 5-MeO, 5-Br) was transformed into the brown powder of [VO(Xsalton)] upon heating at 210 °C for 3−15 h in the air. The reaction proceeded slowly and was accompanied by the formation of a dark brown V(V) unknown byproduct. The thermal dehydrogenation reaction of [VO(Xsal-*meso*-stien)] in the solid state did not occur under

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(14) A figure of electronic spectra of [VO(3-EtOsal-*meso*-stien)] and [VO(3-EtOsalton)] in acetonitrile is deposited in the Supporting Information.

(15) Zamian, J. R.; Dockal, E. R.; Castellano, G.; Oliva, G. *Polyhedron* **1995**, *14*, 2411.

an argon atmosphere. On the other hand, the reaction under an oxygen atmosphere at 210 °C was about 2 times faster than that in the air. The benzylic carbon atoms of the N−N chelate ring of the complexes are oxidized by oxygen in the air to form a C═C double bond and a water molecule (eq 1).

$$[\mathrm{VO}(\mathrm{Xsal}\text{-}meso\text{-}\mathrm{stien})] + {}^{1}/_{2}\mathrm{O}_2 \rightarrow [\mathrm{VO}(\mathrm{Xsalton})] + \mathrm{H}_2\mathrm{O} \quad (1)$$

TG measurement of [VO(3-EtOsal-*meso*-stien)]·H_2O showed a 2.5% weight loss between 52 and 67 °C, which corresponds to 0.82 molecule of water per vanadium. DSC measurement was carried out using an open sample pan of aluminum under nitrogen and oxygen atmospheres. Using nitrogen as a purge gas, two heat absorptions (33 ± 4 and 15 ± 2 kJ mol^{-1}) were observed at 40 ± 5 and 200 ± 2 °C; these endothermic anomalies are irreversible, which was confirmed by repeating the heating and cooling runs. The first anomaly is attributable to the dehydration observed by TG. In addition to these anomalies, a large exothermic anomaly (-150 ± 50 kJ mol^{-1}) was observed around 220 °C using oxygen as a purge gas. An exothermic anomaly peak (-150 ± 50 kJ mol^{-1}) was also recorded when the sample was maintained at 175 or 210 °C in an oxygen atmosphere. This heat emission was completed in 250 min at 175 °C and in 100 min at 210°C. It should be noted that the exothermic anomaly appeared on heating the sample in an oxygen atmosphere but did not occur in a nitrogen atmosphere. This anomaly can be attributed to the dehydrogenation reaction.

The rate of the thermal dehydrogenation reaction in the solid state is influenced by the substituents (X) of [VO(Xsal-*meso*-stien)]. When the electron-donating groups are introduced into the 5- or 3-position of the salicylaldehyde moieties (X = 3-EtO, 5-MeO), the reaction is accelerated. When [VO(Xsal-*meso*-stien)] was heated at 190 °C for 8 h in the solid state, dehydrogenated [VO(Xsalton)] was obtained in 60% yield for X = 5-MeO, in 45% yield for X = 3-EtO, in 22% yield for X = 5-Br, and in ca. 15% yield for X = H. Dehydrogenation reaction did not occur for the 5-NO_2 and 4-MeO substituted complexes, which have electron-withdrawing groups at the 5-position and electron-donating groups at the 4-position, respectively.

When the powder of the ligands H_2(X-sal-*meso*-stien) was heated at 190 °C, only decomposition of the material was observed. [VO{3-EtOsal-(*R*,*R*)-stien}] (H_2{3-EtOsal-(*R*,*R*)-stien} = *N*,*N'*-di-3-ethoxysalicylidene-(*R*,*R*)-1,2-diphenyl-1,2-ethanediamine) was also transformed into [VO(3-EtOsalton)] upon heating in the solid state in the air. However, the reaction proceeded slowly; only 22% of [VO{3-EtOsal-(*R*,*R*)-stien}] was transformed into [VO(3-EtOsalton)] under the same conditions as above (190 °C for 8 h). This fact indicates that the cis configuration of the two hydrogen atoms of the five-membered N−N chelate ring in [VO(3-EtOsal-*meso*-stien)] is preferable for the dehydrogenation reaction to the trans configuration of the hydrogen atoms in [VO{3-EtOsal-(*R*,*R*)-stien}].

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Supporting Information Available: A figure showing electronic spectra of [VO(3-EtOsal-*meso*-stien)] and [VO(3-EtOsalton)] in acetonitrile, ORTEP drawings with numberings of atoms of **1** and **2**, and a crystal structure of **1** (5 pages). X-ray crystallographic files, in CIF format, for compounds **1** and **2** are available on the Internet only. Ordering and access information is given on any current masthead page.

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