Molecular Rearrangement Accompanied by Solid-State Isomerization of {*N*,*N*′-Di-3-ethoxysalicylidene-(*R*,*S*)(*S*,*R*)-1,2-diphenyl-1,2-ethanediamine}oxovanadium(IV)

Gakuse Hoshina, Shigeru Ohba,* Kiyohiko Nakajima,† Hiroyuki Ishida,†† Masaaki Kojima,†† and Masanobu Tsuchimoto

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522

†Department of Chemistry, Aichi University of Education, Igaya, Kariya 448-8542

††Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700-8530

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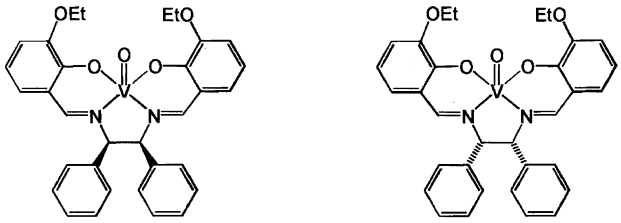
Two geometrical isomers, *exo*- and *endo*-[VO(3-EtOsal-*meso*-stien)] (H_2(3-EtOsal-*meso*-stien) = *N*,*N*′-di-3-ethoxysalicylidene-(*R*,*S*)(*S*,*R*)-1,2-diphenyl-1,2-ethanediamine), were selectively prepared separately. X-Ray structure analyses were carried out for two different crystals of the *endo*-isomer: *endo*-[VO(3-EtOsal-*meso*-stien)]·$3H_2O$, (**A**), monoclinic $P2_1/c$, a = 10.435(3), b = 9.696(3), c = 30.948(3) Å, β = 94.87(2)°, V = 3120(1) Å^3 and Z = 4; *endo*-[VO(3-EtOsal-*meso*-stien)]·CH_3CN, (**B**), monoclinic $P2_1/c$, a = 15.935(3), b = 9.510(2), c = 20.891(2) Å, β = 100.58(1)°, V = 3112(1) Å^3 and Z = 4. Under an argon atmosphere, the *endo*-isomer in both crystals **A** and **B** isomerized to the *exo*-isomer completely upon heating at 210 °C for 20 h. The X-ray powder diffraction patterns of the heated crystals **A**′ and **B**′ were approximately identical with that of *exo*-[VO(3-EtOsal-*meso*-stien)]·H_2O (**C**). In the latter the V=O bonds are arranged in crystals to form a fairly weak linear chain structure (V=O···V=O···). The drastic rearrangement of the metal complexes in the solid state accompanied by the isomerization reaction indicates that the thermal reaction proceeds in a non-topochemical fashion.

Schiff base-oxovanadium(IV) complexes are known to have catalytic properties[1,2] and biological relevances,[3,4] and a considerable number of complexes have been prepared and characterized. The color of most Schiff base-oxovanadium(IV) complexes is green, and they have a monomeric square-pyramidal structure in the solid state. There are also several orange crystals, where complexes are stacked to form a linear V=O···V=O··· chain.[5] Recently, thermal reactions of the Schiff base-oxovanadium(IV) complexes in the solid state have been reported, which include interconversion between the monomeric and polymeric forms of the complexes,[6—8] isomerization of the complexes[9] and dehydrogenation of the Schiff base ligands.[10] The isomerization reaction between a diastereomeric pair of complexes in the solid state upon heating at 195 °C has been reported for [VO{3-EtOsal,sal-(*RR*)-chxn}] (H_2{3-EtOsal,sal-(*RR*)-chxn} = *N*-salicylidene-*N*′-3-ethoxysalicylidene-(*R*,*R*)-1,2-cyclohexanediamine).[9] It is interesting to study the transformation of the crystal structure during the thermal reaction. However, suitable crystals were not available for the X-ray work.

In this study, the relationship between the crystal structures and the thermal isomerization of the title complex was investigated. For this complex, two geometrical isomers, *exo* and *endo*, are possible (Fig. 1). The *exo* and *endo* isomers are defined as that the substituted groups (two phenyl groups) of the central diamine moiety in the Schiff base ligand are both directed outside or inside to the O(oxo)N_2 plane of the VN_2O_3 square pyramid, respectively. Thermal dehydrogenation of the sal-*meso*-stien ligand occurred at benzylic positions upon heating the complex at 210 °C in the solid state in the air by O_2.[10] Under an argon atmosphere, only the thermal isomerization from *endo* to *exo* was observed.



exo *endo*

Fig. 1. Two possible geometrical isomers of [VO(3-EtOsal-*meso*-stien)].

Experimental

The Schiff base ligand H_2(3-EtOsal-*meso*-stien) and the complex *exo*-[VO(3-EtOsal-*meso*-stien)] were prepared according to a reported procedure.[10]

Synthesis of *endo*-[VO(3-EtOsal-*meso*-stien)]. To a dichloromethane solution (30 mL) of H_2(3-EtOsal-*meso*-stien) (0.49 g, 1 mmol) was added a dichloromethane solution (30 mL) of

[VO(acac)$_2$] (H_2acac = 2,4-pentanedione; 0.27 g, 1 mmol). The solution was stirred for 5 h and evaporated to dryness. The resulting green powder was collected and washed with ether. Yield of *endo*-[VO(3-EtOsal-*meso*-stien)]: 0.47 g (95%). Found: C, 66.75; H, 5.35; N, 4.78%. Calcd for $C_{32}H_{30}N_2O_5V$: C, 67.01; H, 5.27; N, 4.89%. IR (KBr) 983 ($\nu_{V=O}$), 1603 cm^{-1} ($\nu_{C=N}$). UV-vis (CH_3CN) $\sigma_{max}/10^3$ cm^{-1} (log ε) 16.3 (2.13), 25.8 (3.70), 34.2 (4.44), 42.5 (4.57).

Crystal Structure Determination. Green crystals of *endo*-[VO(3-EtOsal-*meso*-stien)]·3H_2O (**A**) were grown by slow evaporation from an acetonitrile–water (95 : 5 (v/v)) solution. From a dry acetonitrile solution, green crystals of *endo*-[VO(3-EtOsal-*meso*-stien)]·CH_3CN (**B**) were obtained. The X-ray diffraction data of **A** and **B** were collected at room temperature on a Rigaku AFC-5 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.71073 Å) up to 2θ = 55°. The crystals were coated with an adhesive to prevent efflorescence. The intensity of standard reflections continuously decreased by 12% in $|F_o|$ for (**B**). The intensities were corrected based on the standard reflections. Absorption corrections were made by a numerical-integration method based on the crystal shape. The structures were solved by direct methods and refined using the observed reflections [$|F_o| > 3\sigma(|F_o|)$]. The calculations were performed using CRYSTAN-GM software[11] on a SUN SPARC10 workstation. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were introduced at ideal positions, except for solvent molecules for crystallization. Crystal data and the experimental details are given in Table 1. The atomic coordinates, thermal parameters, bond distances and angles, and $F_o - F_c$ tables are deposited as Document No. 72018 at the office of the Editor of Bull. Chem. Soc. Jpn.

Thermal Isomerization. The *endo*-isomer in green powder samples of **A** and **B** completely isomerized to the *exo*-isomer upon heating at 210 °C for 20 h under an argon atmosphere. The progress of isomerization was followed by a high-performance liquid-chromatographic (HPLC) method with acetonitrile–water (7 : 3 v/v) as an eluent. In this condition, the title complex does not show any isomerization in solution. The thermal products of **A** and **B** (hereafter they are called as **A′** and **B′**) were found to contain water of crystallization. *exo*-[VO(3-EtOsal-*meso*-stien)]·H_2O (**A′**): Found: C, 64.40; H, 5.10; N, 4.75%. Calcd for $C_{32}H_{32}N_2O_6V$: C, 64.97; H, 5.45; N, 4.75%. IR (KBr) 987 (vs, V=O), 1602 cm^{-1} (vs, C=N). *exo*-[VO(3-EtOsal-*meso*-stien)]·H_2O (**B′**): Found: C, 65.18; H, 5.13; N, 4.81%. Calcd for $C_{32}H_{32}N_2O_6V$, same as above. IR (KBr) 987 ($\nu_{V=O}$), 1602 cm^{-1} ($\nu_{C=N}$).

Table 1. Crystallographic Data for *endo*-[VO(3-EtOsal-*meso*-stien)]·3H_2O (**A**) and *endo*-[VO(3-EtOsal-*meso*-stien)]·CH_3CN (**B**)

	A	**B**
Formula	$C_{32}H_{36}N_2O_8V$	$C_{34}H_{33}N_3O_5V$
F.W.	627.59	614.60
Crystal size/mm	0.5 × 0.4 × 0.2	0.6 × 0.3 × 0.1
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	10.435(3)	15.935(3)
b/Å	9.696(3)	9.510(2)
c/Å	30.948(3)	20.891(2)
β/°	94.87(2)	100.58(1)
V/Å^3	3120(1)	3112(1)
Z	4	4
D_{calcd}/Mg m^{-3}	1.336	1.312
μ (Mo $K\alpha$)/mm^{-1}	0.37	0.35
No. of reflections	4212	3880
No. of parameters	418	418
R[a)]	0.066	0.071
R_w[b)]	0.056	0.056

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

Other Measurements. IR spectra were recorded on a JASCO A-202 spectrophotometer by a KBr pellet 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. The X-ray powder-diffraction patterns were measured on a Rigaku RAD-C diffractometer with monochromatized Cu $K\alpha$ radiation (λ = 1.54056 Å).

Results and Discussion

Synthesis. The *exo*-isomer of [VO(3-EtOsal-*meso*-stien)] can be selectively prepared by the reaction of a methanol solution of vanadium(IV)oxysulfate with the Schiff base ligand $H_2$3–EtOsal-*meso*-stien suspended in methanol.[10] The *endo*-isomer was also selectively prepared by the reaction of [VO(acac)$_2$] with the Schiff base ligand in dichloromethane. The $H_2$3-EtOsal-*meso*-stien is soluble in dichloromethane, but is scarcely soluble in methanol. This fact seems to play an important role in the selective preparation of the geometrical isomers of the title complex. IR spectra of the *exo*- and *endo*-isomers showed V=O stretching at 987 and 983 cm^{-1}, respectively, which correspond to monomeric forms in the crystals, consistent with their green colour.[5] The electronic spectrum of the *endo*-isomer is almost identical with that of the *exo*-isomer.

X-Ray Crystal Structures of *endo*-[VO(3-EtOsal-*meso*-stien)]·3H_2O (A) and *endo*-[VO(3-EtOsal-*meso*-stien)]·CH_3CN (B). The *endo*-isomer could be crystallized in two different packing modes. Crystals of trihydrate (**A**) and monoacetonitrile solvate (**B**) were obtained from wet and dry acetonitrile solutions, respectively, and their structures were determined by X-ray analyses. The structure of complex in **A** is shown in Fig. 2. The molecular structure in **B** is approximately identical with that in **A**. Selected bond lengths and bond angles are listed in Table 2. In both crystals **A** and **B**, the geometry around each vanadium atom is a distorted square-pyramid with the oxo ligand, O(2), in the apical position. The V(1)=O(2) bond distance is 1.584(3) Å in **A** and 1.590(3) Å in **B**. The vanadium atom in each complex is displaced by 0.60(1) Å toward the apical oxo ligand from the N_2O_2 basal coordination plane. Two phenyl groups are located on the opposite side of the oxo ligand, and this is the *endo*-isomer. The V–N–C–C(phenyl) torsion angles are 99.5(3) and 178.1(4)° in **A**, and 105.5(4) and 175.5(5)° in **B**. In crystal **A**, one of the water molecules for crystallization (O(41)) is surrounded by four oxygen atoms of the ligand

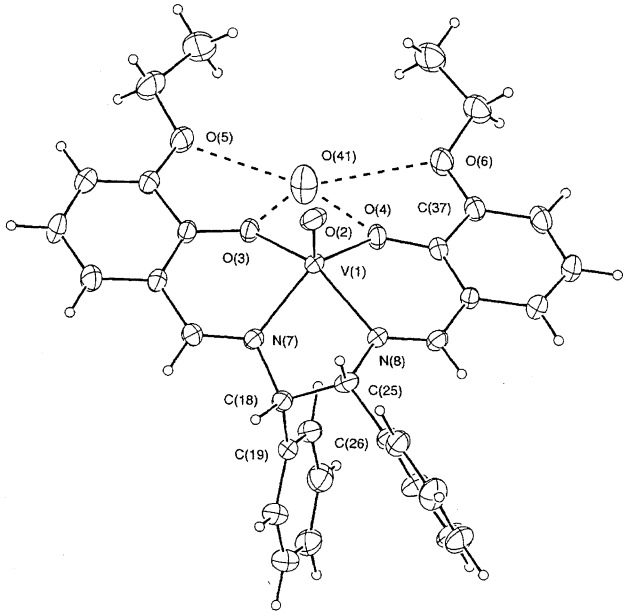


Fig. 2. ORTEP drawing of *endo*-isomer in **A**. The displacement ellipsoids at 20% probability. The O(41) is a water of crystallization, and hydrogen bonds are indicated with broken lines.

Table 2. Selected Bond Lengths (l/Å), Bond Angles (ϕ/°) and Torsional Angles (ϕ/°) of *endo*-[VO(3-EtOsal-*meso*-stien)]·$3H_2O$ (**A**), *endo*-[VO(3-EtOsal-*meso*-stien)]·CH_3CN (**B**), and *exo*-[VO(3-EtOsal-*meso*-stien)]·H_2O (**C**)[10]

	A	B	C
V(1)–O(2)	1.584(3)	1.590(3)	1.597(3)
V(1)–O(3)	1.932(2)	1.927(4)	1.934(2)
V(1)–O(4)	1.929(3)	1.930(3)	1.925(3)
V(1)–N(7)	2.047(3)	2.062(4)	2.072(3)
V(1)–N(8)	2.075(3)	2.050(4)	2.065(3)
O(2)–V(1)–O(3)	106.6(2)	107.6(2)	107.2(2)
O(2)–V(1)–O(4)	113.2(2)	113.2(2)	107.7(1)
O(2)–V(1)–N(7)	106.3(2)	105.6(2)	107.8(1)
O(2)–V(1)–N(8)	103.1(2)	103.4(2)	105.4(1)
N(7)–V(1)–N(8)	78.0(2)	78.4(2)	77.9(1)
N(7)–C(18)–C(25)–N(8)	46.8(3)	43.8(3)	31.6(3)
V(1)–N(7)–C(18)–C(19)	99.5(3)	105.5(4)	−144.1(4)
V(1)–N(8)–C(25)–C(26)	178.1(4)	177.5(5)	92.6(3)

(O(3), O(4), O(5), O(6)) with O···O distances of 2.979(4)—3.061(4) Å (Fig. 2). The O(41) atom is shifted from the O_4 best plane by 1.27 Å at the other side of the oxo O(2) atom. Different syntheses have suggested that two H atoms of O(41) lie between O(3) and O(5), and between O(4) and O(6) to form bifurcated hydrogen bonds. A similar structural feature concerning the encapsulation of a water molecule with two ethoxy substituents at the 3-positions has been observed for other Schiff base-oxovanadium(IV) complexes.[8,10,12] The crystal structures of **A** and **B** are shown in Figs. 3 and 4 with schematic drawings, where the positions and orientations of

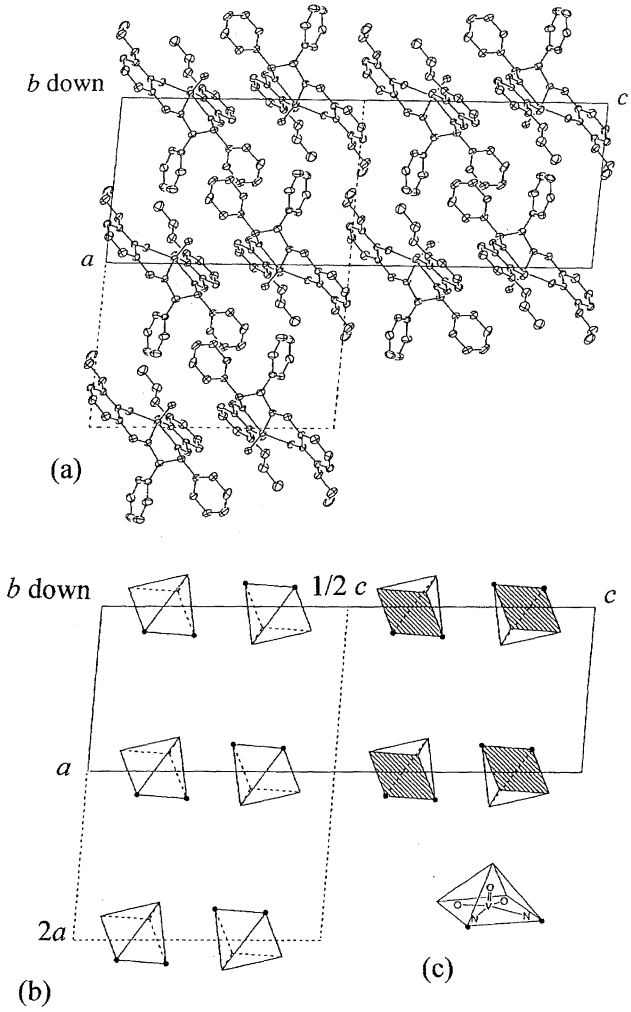


Fig. 3. (a) Projection of the crystal structure of *endo*-[VO(3-EtOsal-*meso*-stien)]·$3H_2O$ (**A**) as viewed down the *b*-axis. Water molecules for crystallization are omitted for clarity. (b) Schematic drawing of the arrangement of the complexes with square-pyramidal coordination. The basal planes of square-pyramids are hatched if they are directed upward. (c) Definition of the square-pyramid, where two corners correspond to the N atoms are closed circles.

the VN_2O_3 square-pyramid are indicated. The crystals of **A** and **B** have similarities. Their lattice constants are roughly related as $a_B \approx 1/2c_A$, $b_B \approx b_A$, and $c_B \approx 2a_A$. In Fig. 3, an artificial cell with $1/2c_A$ and $2a_A$ is shown by broken lines, which well corresponds to the cell with a_B and c_B in Fig. 4. The orientations of half of the complexes in **A** agree with those in **B**, and the other half in **A** are a mirror image with those in **B** to the *ac* plane.

Isomerization Reaction. The *endo*-isomer in crystals **A** and **B** completely isomerized to the *exo*-isomer upon heating at 210 °C for 20 h under an argon atmosphere in the solid state. On the other hand, the isomerization reaction did not proceed in an acetonitrile–water (95 : 5 v/v) solution at 40 °C for 15 h, although certain oxovanadium(IV) complexes isomerize in solution with the presence of water.[13] Progress of the isomerization has been followed by the HPLC method

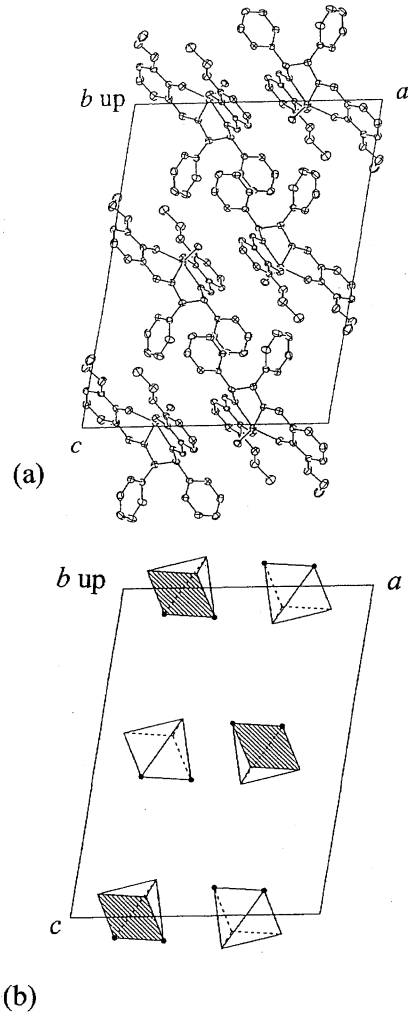


Fig. 4. (a) Projection of the crystal structure of *endo*-[VO(3-EtOsal-*meso*-stien)]·CH_3CN (**B**) as viewed up the *b*-axis. Acetonitrile molecules for crystallization are omitted for clarity. (b) Schematic drawing of the arrangement of the complexes with square-pyramidal coordination.

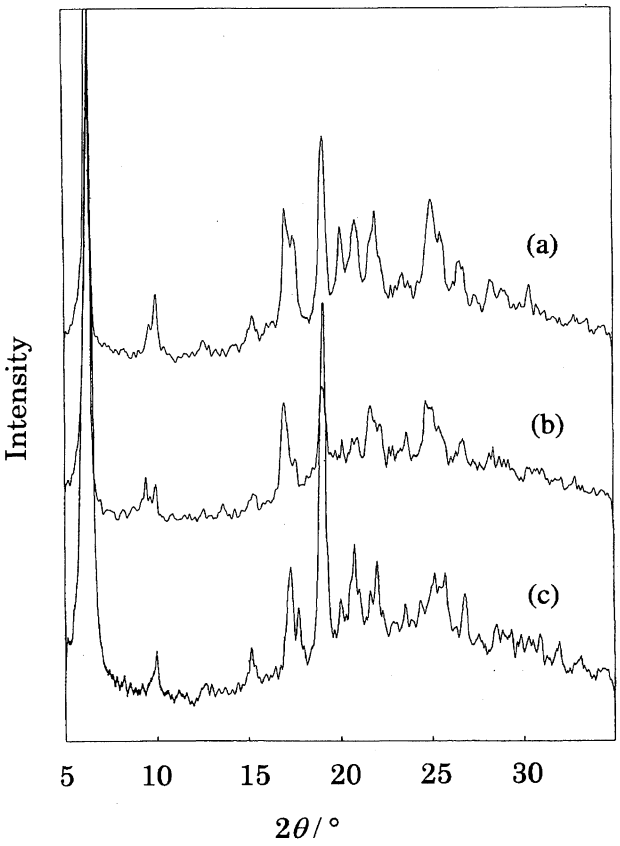


Fig. 5. X-Ray powder diffraction patterns measured with Cu $K\alpha$ radiation. (a) and (b) are the thermal products **A′** and **B′**, respectively. The powder crystals of *endo*-[VO(3-EtOsal-*meso*-stien)]·$3H_2O$ (**A**) and *endo*-[VO(3-EtOsal-*meso*-stien)]·CH_3CN (**B**) were heated at 210 °C for 20 h under argon atmosphere. (c): *exo*-[VO(3-EtOsal-*meso*-stien)]·H_2O (**C**).[10]

with acetonitrile-water used as an eluent. The thermal products, **A′** and **B′**, contained water of crystallization. It seems that the water molecules were incorporated into the crystals at room temperature under the air after heating.

A DSC measurement of crystal **A** was carried out with a heating rate of 0.1 °C min^{-1} from 160 to 260 °C under an argon atmosphere. Water molecules for crystallization seemed to be removed below 100 °C during the preheating.[8,10] Heat absorption (13±2 kJ mol^{-1}) was observed in the temperature range 225—245 °C. The complete thermal conversion of the DSC sample from *endo* to *exo* was confirmed by the HPLC method. The crystals did not melt below 260 °C. Crystals **A** and **B** show efflorescence in the air. A TG measurement was not carried out.

The X-ray powder-diffraction profiles of thermal products **A′** and **B′** yielded by the heating of **A** and **B**, respectively, at 210 °C for 20 h are shown in Fig. 5. Both patterns of **A′** and **B′** are approximately identical with that of *exo*-[VO(3-EtOsal-*meso*-stien)]·H_2O (**C**), whose structure was previously reported.[10] The crystal structure of **C** is shown in Fig. 6 for a comparison. The space group is $P2_1/n$, and the V=O bonds lie nearly on the 2_1 screw axis parallel to *b* to form a fairly weak linear-chain structure. The intermolecular V···O distance is 4.060(2) Å and the O···V=O angle is 153.6(2)°. The *exo*-metal complexes in **C** are more closely packed than the *endo*-isomers in **A** and **B**. The density of **C**, 1.357 Mg m^{-3}, is greater than those of crystals **A** (1.336 Mg m^{-3}) and **B** (1.312 Mg m^{-3}).

The crystal transformations from **A** and **B** to **C** accompany a drastic rearrangement of the oxovanadium complexes. Although the solvent molecules for crystallization may be easily lost upon heating below 100 °C, and there may be some void in the crystals, such a drastic molecular rearrangement will not be topochemical.[14] The intramolecular strain energies of the *exo*- and *endo*-isomers seem to be similar, since both isomers could be selectively prepared under mild conditions. The difference in the lattice energies of the crystals will be important in determining the relative stability of the geometrical isomers in the solid state. There may be an equilibrium between the *endo*- and *exo*-isomers at high temperature. Under these conditions, the free energy of the anhydrate form of crystal **C** may be less than those of **A** and **B**, and the

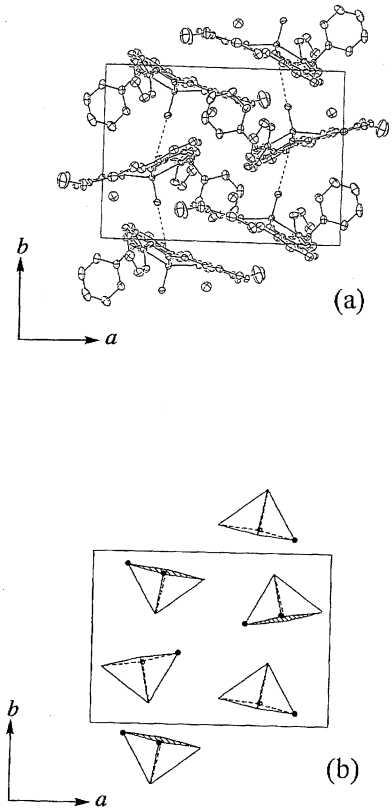


Fig. 6. Projection of the crystal structure of *exo*-[VO(3-EtOsal-*meso*-stien)]·H_2O (**C**) as viewed up the *c*-axis.[10] (b) Schematic drawing of the arrangement of the complexes with square-pyramidal coordination.

nucleation and crystallization of **C** seems to occur in a non-topochemical fashion.

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