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Green and Orange Crystalline Forms of [VO{*N*-salicylidene-*N'*-3-ethoxysalicylidene-(*R,R*)-1,2-cyclohexanediamine}], Separation of the Diastereomeric Pair, and Isomerization between Them in the Solid State

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A pair of diastereomers, I and II, of the titled complex were separated by liquid chromatography, and each of them crystallized in two different colors, green and orange. I(green) and II(green) were assigned to a mononuclear square pyramidal structure, while I(orange) and II(orange) to a polynuclear linear chain structure. The orange complexes turned green by heating at 195 °C in a few minutes. All of the four complexes undergo isomerization at 195 °C in the solid state to give an equilibrium mixture, I : II ≈ 1 : 1.

Most oxovanadium(IV) complexes have square pyramidal structures, and the V=O bond is stable and inert.[1] The present oxovanadium(IV) complex with a tetradentate Schiff base ligand derived from salicylaldehyde, 3-ethoxysalicylaldehyde, and (*R,R*)-1,2-cyclohexanediamine can have a pair of diastereomers, I and II in Fig. 1. The isomers can isomerize to each other by changing the disposition of the V=O group with respect to the complex basal plane. In this letter, we report the preparation of these two isomers and novel isomerization in the solid state between them.

A methanol solution (20 cm^3) containing salicylaldehyde (5 mmol), 3-ethoxysalicylaldehyde (5 mmol), and (*R,R*)-1,2-cyclohexanediamine (5 mmol) was kept at 30 °C for 15 min. To the resulting yellow solution was added a hot (*ca.* 60 °C) methanol solution (20 cm^3) of $VOSO_4 \cdot 5H_2O$ (5 mmol), and then water (20 cm^3). The mixture was ice-cooled to yield a green precipitate. Yield: 1.5 g. The precipitate was dissolved in dichloromethane and subjected to silica gel column chromatography (eluent: dichloromethane-ethyl acetate (93:7 v/v)). The column showed four green bands. The fastest-moving band was [VO{sal,sal-(*RR*)-chxn}], and the slowest-moving one was [VO{3-EtOsal,3-EtOsal-(*RR*)-chxn}].[2] Each eluate containing the second and the third bands was evaporated at *ca.* 30 °C to dryness under reduced pressure to yield isomers I and II, respectively, of [VO{3-EtOsal,sal-(*RR*)-chxn}]. They were obtained as a mixture of green and orange microcrystals. The isomerization reaction between isomers I and II does not take place under these conditions. Green crystals of I and II were obtained by recrystallization of the respective crude products from dichloromethane. Found for I(green): C, 58.09; H, 5.35; N, 6.01%. Calcd for [VO{3-EtOsal,sal-(*RR*)-chxn}]·

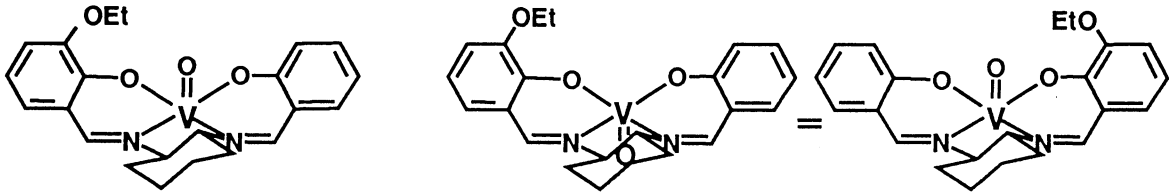

Fig. 1. Two possible diastereomers of [VO{3-EtOsal,sal-(*RR*)-chxn}].

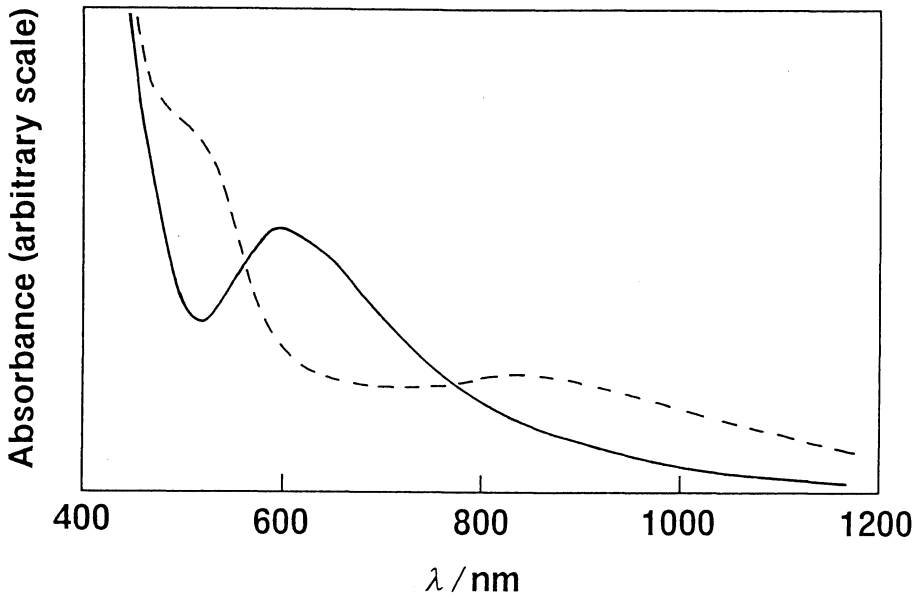

Fig. 2. Reflection spectra of isomers I(green) (——) and I(orange)(– – –) of [VO{3-EtOsal,sal-(*RR*)-chxn}].

$1.5H_2O$=$C_{22}H_{27}N_2O_{5.5}V$: C, 57.64; H, 5.93; N, 6.11%. Found for II(green): C, 59.33; H, 5.34; N, 6.08%. Calcd for [VO{3-EtOsal,sal-(*RR*)-chxn}]·H_2O=$C_{22}H_{26}N_2O_5V$: C, 58.90; H, 5.83; N, 6.23%. Orange crystals (I and II) were obtained by suspending the green crystals (0.1 g) of the respective isomers in acetonitrile-water (1:2 v/v, 50 cm^3) under nitrogen. Found for I(orange): C, 57.69; H, 5.62; N, 5.49%. Found for II(orange): C, 57.38; H, 5.40; N, 5.89%. Calcd for [VO{3-EtOsal,sal-(*RR*)-chxn}]·$1.5H_2O$= $C_{22}H_{27}N_2O_{5.5}V$: C, 57.64; H, 5.93; N, 6.11%. The thermogravimetric analyses of the four complexes, I(green), II(green), I(orange), and II(orange), show that water of crystallization is lost easily at 110 °C. Since we have not obtained crystals suitable for X-ray structure analysis, we do not know which of the two structures in Fig. 1 should be assigned to isomer I.

For the present type of complex, it is known that a five-coordinate square pyramidal species is blue or green, while a six-coordinate polymer, in which an infinite chain of molecules connected by ···V=O···V=O··· bonds exists, is orange or red.[3] We assign the green complexes to a square pyramidal five-coordinate geometry and the orange complexes to a linear chain structure. The infrared spectra support the assignments; the orange complexes show the V=O stretching at a lower frequency (*ca.* 875 cm^{-1}) than that of the green complexes (*ca.* 990 cm^{-1}). The reduction in the V=O stretching frequency in the orange complexes is attributable to the weakening of the V=O bond by forming ···V=O···V=O··· bonds. To our knowledge, the present complex is the first example of a Schiff base-oxovanadium(IV) complex to have the two stable forms, green and orange, at room temperature.[4] Figure 2 shows the reflection spectra of complexes I(green) and

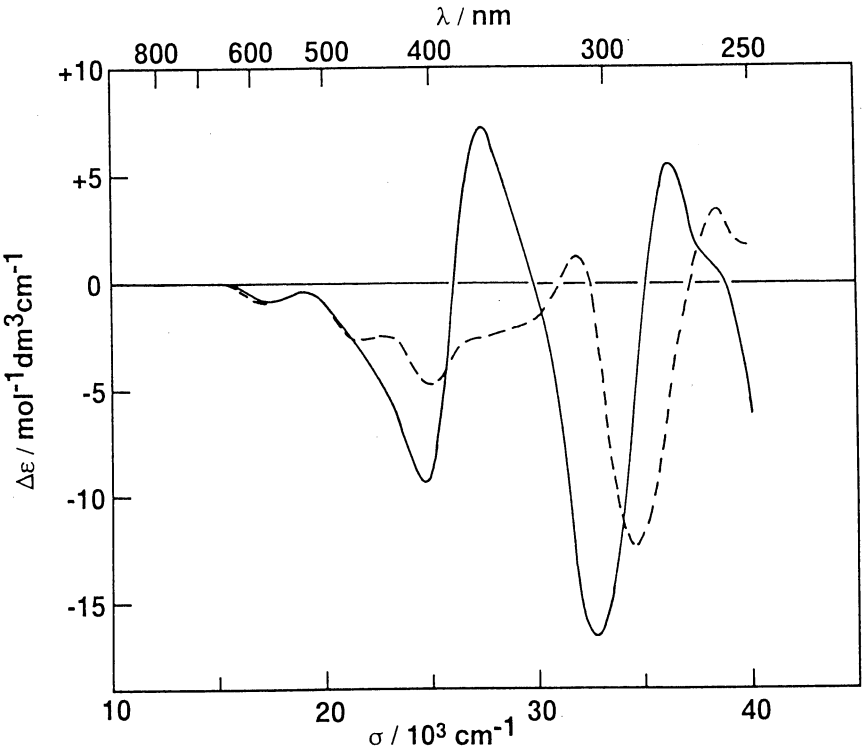

Fig. 3. CD spectra of isomer I (———) and Isomer II (– – –) of [VO{3-EtOsal,sal-(*RR*)-chxn}] in dichloromethane.

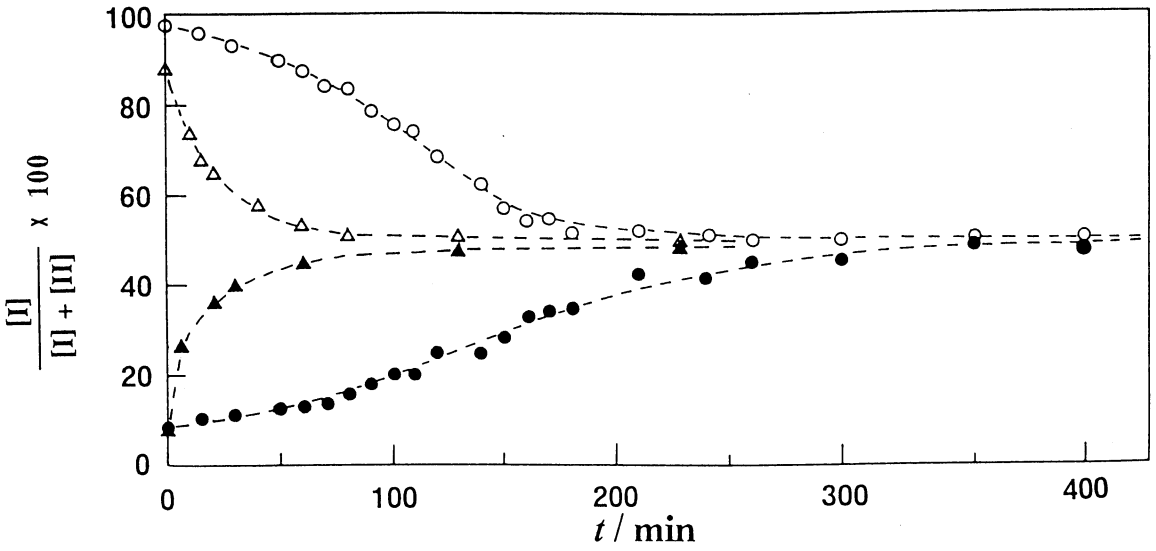

Fig. 4. Reaction profile of the isomerization reaction of [VO{3-EtOsal,sal-(*RR*)-chxn}] at 195 °C: △, I(orange); ▲, II(orange); ○, I(green); ●, II(green).

I(orange). Orange complexes I and II turn green immediately upon dissolution in common solvents such as dichloromethane and acetonitrile, and the absorption spectra are identical, respectively, with those of green complexes I and II. Thus, both orange complexes I and II change to a monomeric structure in solution. Little difference in absorption spectra is observed between isomers I and II in dichloromethane. On the other hand, the

circular dichroism spectra are significantly different between isomers I and II in the region of charge-transfer transitions (Fig. 3).

The four complexes, I(green), II(green), I(orange), and II(orange), were heated in an oven at 195 °C in the solid state. The progress of the solid-state isomerization reaction between isomers I and II at 195 °C was followed by a high-performance liquid chromatographic method. Portions of the complexes were taken out from the oven at timed intervals, dissolved in acetonitrile, and then chromatographed on a column (ø0.46 cm x 15 cm) of JASCO CrestPak C18S with CH_3CN-H_2O (44:56 v/v) as an eluent. The two isomers, I and II, in the eluate were detected at 250 nm, where they have the same molar absorption coefficients. Figure 4 shows the percentage of isomer I against reaction time. We have confirmed that no isomerization reaction between the two isomers, I and II, takes place in the process of isomer distribution analyses. The reactions were carried out in air and in an atmosphere of nitrogen, and there was no difference between the results. The orange complexes, I(orange) and II(orange), isomerize rather fast at 195 °C, and after 1 h, the reactions attain equilibrium, I : II ≈ 1 : 1. The orange complexes have a linear chain structure, and the isomerization reaction might take place by migration of the terminal oxygen (V=O) to the adjacent vanadium. However, the reactions were accompanied by a color change; the orange complexes turned green within a few minutes at 195 °C, indicating the disassembling of the chain structure. Thus, the stable form of the complexes at high temperature is the green one. Cooling the green complexes to 0 °C does not produce a color change. It should be noted that the isomerization reaction proceeds even after the complexes disassembled to monomeric five-coordinate green complexes, where there will be no vanadium in the neighborhood of the terminal oxygen atom. The green complexes, I(green) and II(green), isomerize more slowly than the orange complexes, and no color change was observed. Thus, the green complexes formed by heating the orange complexes seem to have different crystal structures from those of the original green complexes, I(green) and II(green). In order to study the isomerization mechanism, it is necessary to have a detailed knowledge of the crystal structures, and we are now trying to obtain good crystals suited for X-ray analyses.

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References

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2) H_2{sal,sal-(*RR*)-chxn} and H_2{3-EtOsal,3-EtOsal-(*RR*)-chxn} denote *N,N'*-disalicylidene-(*R,R*)-1,2-cyclohexanediamine and *N,N'*-di-3-ethoxysalicylidene-(*R,R*)-1,2-cyclohexanediamine, respectively.

3) M. Mathew, A. J. Carty, and G. J. Palenik, *J. Am. Chem. Soc.*, **92**, 3197 (1970); A. Serrette, P. J. Carroll, and T. M. Swager, *J. Am. Chem. Soc.*, **114**, 1887 (1992); K. Nakajima, K. Kojima, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 2620 (1990).

4) Pasini and Gullotti[5] obtained [VO{sal-(-)-stien}] (H_2{sal-(-)-stien} = *N,N'*-disalicylidene-(-)-1,2-diphenyl-1,2-diaminoethane) as a yellow-brown powder, which turns green upon grinding. However, the green form was not stable and became brown, and they could not record its reflection spectrum.

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