

Mechanochemical Reaction of Polymeric Oxovanadium(IV) Complexes with Schiff Base Ligands Derived from 5-Nitrosalicylaldehyde and Diamines

Masanobu Tsuchimoto,^{*1} Gakuse Hoshina,^{*} Naoki Yoshioka,[†] Hidenari Inoue,[†] Kiyohiko Nakajima,[‡] Mayumi Kamishima,[§] Masaaki Kojima,[§] and Shigeru Ohba^{*}

^{*}Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan;

[†]Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan;

[‡]Department of Chemistry, Aichi University of Education, Igaya, Kariya 448-8542, Japan; and [§]Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700-8530, Japan

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Light brown $[\text{VO}(\text{5-NO}_2\text{salen})] \cdot 2\text{H}_2\text{O}$ (**1**; $\text{H}_2(\text{5-NO}_2\text{salen}) = N, N'$ -di-5-nitrosalicylidene-1,2-ethanediamine) and orange $[\text{VO}(\text{5-NO}_2\text{sal-meso-stien})] \cdot 0.5\text{H}_2\text{O}$ (**2**; $\text{H}_2(\text{5-NO}_2\text{sal-meso-stien}) = N, N'$ -di-5-nitrosalicylidene-(*R,S*)(*S,R*)-1,2-diphenyl-1,2-ethanediamine) which have linear chain structures in the solid state turn dark brown and yellow-brown, respectively, when ground thoroughly in mortars. The IR spectra of **1** and **2** in Nujol mulls show strong $\text{V}=\text{O}$ stretching bands at 875 and 905 cm^{-1} , respectively. On the other hand, the spectra of the finely ground complexes in Nujol mulls show very weak $\text{V}=\text{O}$ stretching bands. X-ray powder diffraction patterns of the ground complexes scarcely show diffraction peaks. The spectroscopic and magnetic data suggest that the linear chain structures in the crystals of **1** and **2** are destroyed on grinding to yield the fragments of the polymeric chains. © 2000 Academic Press

Key Words: mechanochemical reaction; polymeric complex; oxovanadium(IV) complex.

INTRODUCTION

Oxovanadium(IV) complexes with tetradentate Schiff base ligands have green monomeric structures with square-pyramidal coordination or orange linear chain structures ($\dots \text{V}=\text{O} \dots \text{V}=\text{O} \dots$) with distorted octahedral coordination in the solid state (**1**). IR spectra of these complexes show the $\text{V}=\text{O}$ stretching bands around 960–990 cm^{-1} for monomeric ones, and around 850–880 cm^{-1} for polymeric ones. Recently, we reported interconversions between monomeric and polymeric forms of oxovanadium(IV) complexes in the solid state which occur upon heating or grinding of the complexes (**2**–**4**).

¹To whom correspondence should be addressed. Fax: +81-45-566-1697. E-mail: tmoto@chem.keio.ac.jp.

Oxovanadium(IV) complexes with Schiff base ligands derived from 5-nitrosalicylaldehyde and diamines, $[\text{VO}(\text{5-NO}_2\text{salen})] \cdot 2\text{H}_2\text{O}$ (**1**; $\text{H}_2(\text{5-NO}_2\text{salen}) = N, N'$ -di-5-nitrosalicylidene-1,2-ethanediamine) and $[\text{VO}(\text{5-NO}_2\text{sal-meso-stien})] \cdot 0.5\text{H}_2\text{O}$ (**2**; $\text{H}_2(\text{5-NO}_2\text{sal-meso-stien}) = N, N'$ -di-5-nitrosalicylidene-(*R,S*)(*S,R*)-1,2-diphenyl-1,2-ethanediamine) (Fig. 1), form linear chain structures in the solid state (**5,6**). The IR spectra of these complexes in Nujol mulls showed a strong $\text{V}=\text{O}$ stretching band at 875 cm^{-1} for **1** and 905 cm^{-1} for **2**. However, the intensity of the bands significantly decreased when the spectra were measured in KBr disks (Figs. 2 and 3). The light brown complex **1** and the orange complex **2** turned to a dark brown complex **1g** and a yellow-brown complex **2g**, respectively, when they were ground thoroughly in mortars. The IR spectra of **1g** and **2g** in Nujol mulls also showed very weak $\text{V}=\text{O}$ stretching bands. These facts suggest that some mechanochemical reaction occurred on grinding of the complexes. In this report, the mechanism of the reaction will be discussed on the basis of the spectroscopic and magnetic properties of the complexes. The abbreviations **1g**, **2g**, **1gs**, and **1h** are used for the complexes **1** and **2** ground in mortars (**1g** and **2g**), the complex **1** suspended in acetonitrile after grinding (**1gs**), and the complex **1** heated at 130°C for 1 h (**1h**).

EXPERIMENTAL

All organic solvents were reagent grade and used without purification. $[\text{VO}(\text{5-NO}_2\text{sal-meso-stien})] \cdot 0.5\text{H}_2\text{O}$ (**2**) was prepared by the literature method (**6**). Oxovanadium(IV) complexes with Schiff base ligands derived from 5-nitrosalicylaldehyde and related diamines (1,2-propanediamine, 1,3-propanediamine, *rac*- and *meso*-1,2-cyclohexanediamine, etc.) were prepared by a method similar to that used for **1**.



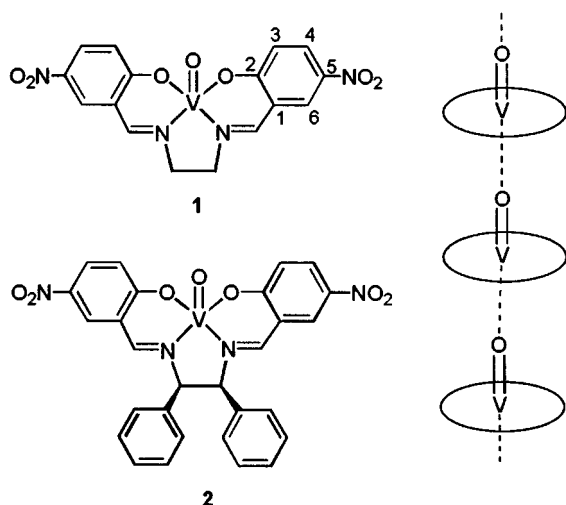


FIG. 1. Polymeric $[\text{VO}(5\text{-NO}_2\text{salen})]$ (**1**) and $[\text{VO}(5\text{-NO}_2\text{sal-meso-stien})]$ (**2**).

Synthesis

$[\text{VO}(5\text{-NO}_2\text{salen})] \cdot 2\text{H}_2\text{O}$ (**1**). To a hot methanol solution (150 cm^3) of vanadyl sulfate (2.53 g, 10 mmol) was added a methanol solution (50 cm^3) of the ligand H_2 (5- NO_2salen) (3.58 g, 10 mmol) and pyridine (10 cm^3), and the mixture was stirred. The resulting light brown precipitate was collected by filtration and washed with methanol.

$[\text{VO}(5\text{-NO}_2\text{salen})] \cdot \text{H}_2\text{O}$ (**1h**). A monohydrate complex $[\text{VO}(5\text{-NO}_2\text{salen})] \cdot \text{H}_2\text{O}$ (**1h**) was prepared upon heating of **1** at 130°C for 1 h and leaving it to stand in the air.

Structure Determination

Crystal data of $[\text{VO}(5\text{-NO}_2\text{sal-meso-stien})] \cdot 0.5\text{H}_2\text{O}$ (**2**). $\text{C}_{28}\text{H}_{21}\text{N}_4\text{O}_{7.5}\text{V}_1$, $M = 584.44$, monoclinic, space group $C2/c$ (No. 15), $a = 30.77(1)$, $b = 7.934(2)$, and $c = 27.02(1) \text{ \AA}$, $\beta = 123.22(2)^\circ$, $U = 5519(4) \text{ \AA}^3$, $Z = 8$, $D_c = 1.41 \text{ g cm}^{-3}$, $F(000) = 2400.0$, $\mu = 4.14 \text{ cm}^{-1}$, crystal size = $0.10 \times 0.20 \times 0.40 \text{ mm}^3$, 6488 reflections measured, 6372 unique reflections, $R = 0.061$, $R_w = 0.101$, $S = 1.488$.

Red prismatic crystals of **2** were obtained by slow diffusion of diethyl ether and methanol vapor into a DMSO solution of **2**. The intensity data were collected at 298 K on a Rigaku AFC-7R diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) up to $2\theta = 55^\circ$ by ω scans. Absorption correction was made by the numerical integration method from crystal shape. The structure was solved by direct methods on a Silicon Graphics O^2 workstation with the program system TEXSAN (7). The oxygen atom of water of crystallization was located on a twofold axis. Nonhydrogen atoms were treated anisotropically, and hydrogen atoms attached to carbon atoms

were introduced at ideal positions. Refinement was based on F with $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w^{-1} = \sigma^2(|F_o|) + 0.00063|F_o|^2$, against all the 6372 reflections. The R value ($\sum ||F_o| - |F_c|| / \sum |F_o|$) was 0.061 for the 3058 reflections with $I > 2\sigma(I)$. Atomic parameters are listed in Table 1.

Measurements

IR spectra were recorded on a JASCO A-202 spectrophotometer by a Nujol mull and a KBr method. KBr disks were prepared as follows. About 40 mg of KBr and 0.2 mg of a sample were finely ground in a mortar for a few minutes. A disk of 3 mm diameter was prepared on pressing about 10

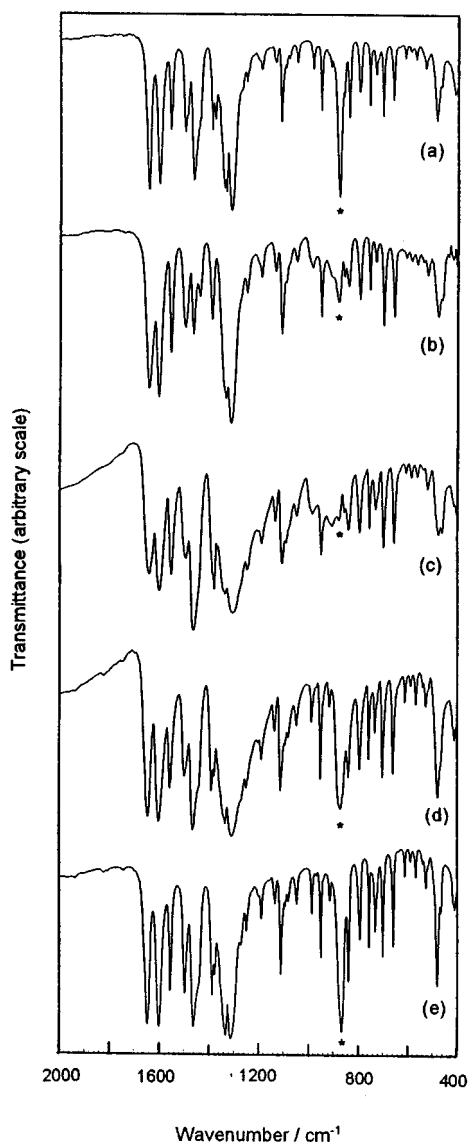


FIG. 2. IR spectra of (a) **1** in a Nujol mull, (b) **1** in a KBr disk, (c) **1g** in a Nujol mull, (d) **1gs** in a Nujol mull, and (e) **1h** in a Nujol mull. The V=O stretching bands are shown in the figures with asterisks.

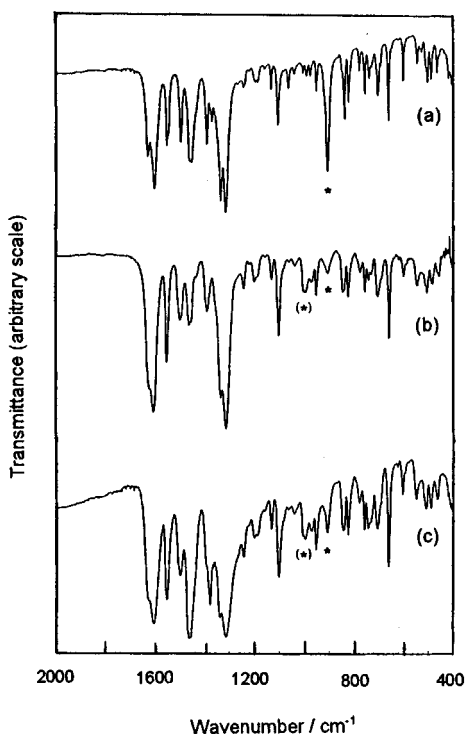


FIG. 3. IR spectra of (a) **2** in a Nujol mull, (b) **2** in a KBr disk, and (c) **2g** in a Nujol mull. The V=O stretching bands are shown in the figures with asterisks.

mg of the ground sample at 5000 N cm^{-2} for a few seconds. Electronic spectra in the solid state were recorded on a JASCO V-570 spectrophotometer by a Nujol mull method (8). X-ray powder diffraction (XRD) patterns were measured on a Rigaku RAD-C diffractometer with monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The temperature dependence of magnetic susceptibilities in the range 1.8 to 300 K was measured on a SQUID magnetometer (Quantum Design MPMS5) at 500 mT. Grinding of the complexes with a ball-mill (Nara machinery AGO-II planetary ball-mill) was carried out as follows. Sixteen zircona balls (10 mm diameter) and 0.5 g of a sample were put into a 27 cm^3 zirconia-lined vessel. Mechanical treatment was carried out at 300 rpm for 1 h under an argon atmosphere. The vessel was cooled with water during the treatment.

RESULTS AND DISCUSSION

A light brown polymeric oxovanadium(IV) complex $[\text{VO}(\text{5-NO}_2\text{salen})] \cdot 2\text{H}_2\text{O}$ (**1**), which is scarcely soluble in solvents, was prepared as the dihydrate by reaction of the Schiff base ligand with vanadyl sulfate in methanol (9). The light brown complex **1** turned to a dark brown complex **1g** when it was ground thoroughly in a mortar in the air. The dark brown complex **1g** turned to a red complex **1gs** after being suspended in acetonitrile for 2 days. A monohydrate

TABLE 1
Fractional Coordinates and Thermal Parameters for **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a, \text{\AA}^2$
V1	0.25173(3)	0.19959(9)	0.25166(3)	0.0384(2)
O2	0.2638(1)	0.3969(4)	0.2625(1)	0.0481(9)
O3	0.2262(1)	0.1850(4)	0.1683(1)	0.0448(8)
O4	0.1813(1)	0.1850(4)	0.2344(1)	0.0455(9)
O5	0.2891(2)	-0.0306(10)	-0.0043(2)	0.178(3)
O6	0.3583(3)	-0.111(1)	0.0776(2)	0.182(3)
O7	0.0540(2)	-0.0315(9)	0.3390(3)	0.145(3)
O8	0.1297(2)	-0.1252(8)	0.4086(2)	0.124(2)
O41	0.5000	0.006(4)	0.2500	0.55(2)
N9	0.3222(1)	0.1005(4)	0.2744(1)	0.0390(10)
N10	0.2802(1)	0.1197(4)	0.3363(1)	0.0402(10)
N11	0.3151(3)	-0.046(1)	0.0498(3)	0.132(3)
N12	0.1009(3)	-0.0552(9)	0.3610(3)	0.103(2)
C13	0.2484(2)	0.1305(6)	0.1424(2)	0.046(1)
C14	0.2205(2)	0.1350(7)	0.0796(2)	0.064(2)
C15	0.2414(3)	0.0803(9)	0.0496(2)	0.084(2)
C16	0.2913(3)	0.0143(8)	0.0808(2)	0.080(2)
C17	0.3204(2)	0.0062(7)	0.1413(2)	0.064(2)
C18	0.3001(2)	0.0675(6)	0.1735(2)	0.052(1)
C19	0.3327(2)	0.0503(6)	0.2368(2)	0.046(1)
C20	0.3572(2)	0.0369(5)	0.3364(2)	0.040(1)
C21	0.4149(2)	0.0648(6)	0.3629(2)	0.048(1)
C22	0.4352(2)	0.1850(9)	0.3448(3)	0.086(2)
C23	0.4889(3)	0.201(1)	0.3716(4)	0.122(3)
C24	0.5211(3)	0.094(2)	0.4141(4)	0.129(4)
C25	0.5030(3)	-0.023(1)	0.4350(4)	0.121(3)
C26	0.4492(2)	-0.0385(8)	0.4086(3)	0.083(2)
C27	0.3384(2)	0.1057(6)	0.3754(2)	0.046(1)
C28	0.3641(2)	0.2652(6)	0.4098(2)	0.051(1)
C29	0.3721(2)	0.4059(7)	0.3851(3)	0.078(2)
C30	0.3988(3)	0.5402(8)	0.4187(4)	0.121(3)
C31	0.4181(4)	0.545(1)	0.4765(4)	0.132(4)
C32	0.4092(3)	0.416(1)	0.5030(3)	0.114(3)
C33	0.3815(2)	0.2701(9)	0.4696(2)	0.085(2)
C34	0.2537(2)	0.0703(5)	0.3570(2)	0.043(1)
C35	0.1974(2)	0.0676(6)	0.3249(2)	0.048(1)
C36	0.1759(2)	0.0064(7)	0.3556(2)	0.058(2)
C37	0.1223(2)	0.0032(8)	0.3275(3)	0.072(2)
C38	0.0897(2)	0.0618(8)	0.2707(3)	0.072(2)
C39	0.1100(2)	0.1188(7)	0.2395(2)	0.061(2)
C40	0.1646(2)	0.1252(6)	0.2660(2)	0.046(1)
H14	0.1850	0.1772	0.0580	0.07(1)
H15	0.2220	0.0882	0.0068	0.11(1)
H17	0.3561	-0.0397	0.1633	0.07(1)
H19	0.3659	-0.0066	0.2527	0.08(1)
H20	0.3530	-0.0830	0.3346	0.10(1)
H22	0.4111	0.2532	0.3117	0.11(1)
H23	0.5022	0.2858	0.3573	0.14(1)
H24	0.5581	0.1061	0.4305	0.09(1)
H25	0.5273	-0.0977	0.4682	0.228(7)
H26	0.4351	-0.1241	0.4222	0.230(7)
H27	0.3461	0.0198	0.4041	0.04(1)
H29	0.3582	0.4022	0.3430	0.11(1)
H30	0.4028	0.6411	0.3979	0.12(1)
H31	0.4398	0.6376	0.5005	0.199(9)
H32	0.4214	0.4278	0.5440	0.12(1)
H33	0.3756	0.1750	0.4881	0.157(10)
H34	0.2726	0.0314	0.3973	0.08(1)
H36	0.1988	-0.0301	0.3968	0.04(1)
H38	0.0523	0.0538	0.2526	0.09(1)
H39	0.0865	0.1634	0.1995	0.06(1)

$$^a U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

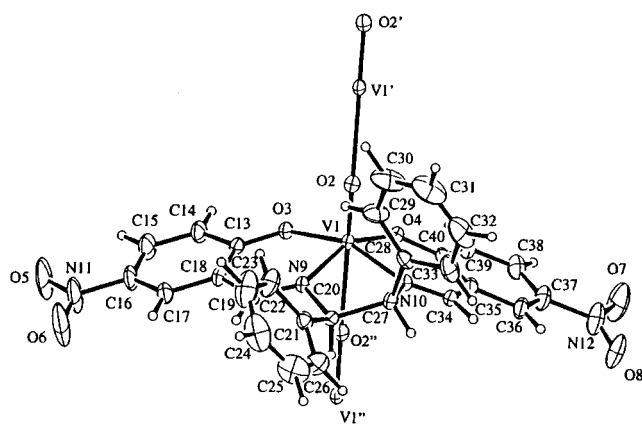


FIG. 4. ORTEP drawing of **2** with 20% probability ellipsoids.

complex $[\text{VO}(5\text{-NO}_2\text{salen})] \cdot \text{H}_2\text{O}$ (**1h**) was obtained upon heating of **1** at 130°C for 1 h and leaving it to stand in the air. An orange polymeric oxovanadium(IV) complex $[\text{VO}(5\text{-NO}_2\text{sal-meso-stien})] \cdot 0.5\text{H}_2\text{O}$ (**2**) also turned to a yellow-brown complex **2g** upon being ground thoroughly in a mortar. The ground complex **2g** was reverted to **2** by suspending it in acetonitrile for 2 h.

Crystals suitable for X-ray structure analysis were not obtained for **1**, but were obtained for **2**. Figure 4 shows the molecular structure of **2**. Selected bond lengths and angles are listed in Table 2. Complex **2** forms a polymeric structure with a distorted octahedral coordination geometry. The $\cdots\text{V}=\text{O}\cdots\text{V}=\text{O}\cdots$ chains run along the 2_1 screw axes parallel to the b axis. The $\text{V}=\text{O}$ units in the linear chain of **2** are more weakly bonded to each other than those of other polymeric Schiff base-oxovanadium(IV) complexes. The $\text{V1}=\text{O2}$ distance ($1.599(3)\text{ \AA}$) is shorter and the $\text{V1}\cdots\text{O2}'$ distance ($2.437(3)\text{ \AA}$) longer than those of polymeric $[\text{VO}(\text{saltn})]$ (H_2saltn : N,N' -disalicylidene-1,3-propanediamine; $\text{V}=\text{O}$ distance $1.633(9)\text{ \AA}$, and $\text{V}\cdots\text{O}$ distance $2.213(9)\text{ \AA}$) (**1**). The IR spectrum of **2** in a Nujol mull shows a $\text{V}=\text{O}$ stretching band at 905 cm^{-1} , which is at higher frequency than those of $[\text{VO}(\text{saltn})]$ (854 cm^{-1}) and **1** (875 cm^{-1}).

TABLE 2
Selected Bond Lengths (\AA) and Angles ($^\circ$) in **2**^a

V1–O2	1.599(3)	V1–O3	1.938(3)
V1–O4	1.955(3)	V1–N9	2.060(4)
V1–N10	2.051(3)	V1–O2'	2.437(3)
O2–V1–O3	100.2(1)	O2–V1–O4	102.5(1)
O2–V1–N9	102.7(1)	O2–V1–N10	100.5(1)
O3–V1–O4	91.7(1)	O3–V1–N9	90.7(1)
O3–V1–N10	158.5(1)	O4–V1–N9	153.8(1)
O4–V1–N10	89.3(1)	N9–V1–N10	79.3(1)
V1–O2–V1'	158.5(2)	O2'–V1–O2	178.2(1)

^aPrimed atoms are generated by $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The V1 atom is displaced by $0.398(2)\text{ \AA}$ from the O3O4N9N10 coordination plane. The five-membered chelate ring takes a distorted gauche conformation with two phenyl groups located on the same side of the oxo ligand (O2). There are two possible geometrical isomers arising from the mutual disposition of the oxo ligand and the two phenyl groups for $[\text{VO}(5\text{-NO}_2\text{sal-meso-stien})]$. Complex **2** is an *exo*-isomer (**10**).

IR spectra of the complexes are shown in Figs. 2 and 3. It is known that IR spectra of tetradentate Schiff base-oxovanadium(IV) complexes generally show the $\text{V}=\text{O}$ stretching band around 970 cm^{-1} for a monomeric form and around 860 cm^{-1} for a linear chain polymeric form. The spectra of **1** and **2** in Nujol mulls showed a strong $\text{V}=\text{O}$ stretching band at 875 cm^{-1} and 905 cm^{-1} , respectively, in accord with the polymeric structures. However, the intensities of the $\text{V}=\text{O}$ stretching bands significantly decreased when the spectra of these complexes were measured in KBr disks. The spectra of **1g** and **2g** in Nujol mulls also showed very weak $\text{V}=\text{O}$ stretching bands. The spectrum of **1g** is similar to that of **1** in a Nujol mull except for a significant decrease in intensity of the $\text{V}=\text{O}$ stretching band and broadening of all the bands. On the other hand, a weak new band (shown with asterisks in parentheses in Figs. 3b, 3c) appeared at 996 cm^{-1} in the spectrum of **2g** in a Nujol mull. These results indicate that grinding of the samples causes a significant decrease in the intensity of the $\text{V}=\text{O}$ stretching bands. The grinding process is also involved in preparing KBr disks. It is to be noted that a decrease in the intensity of the $\text{V}=\text{O}$ stretching bands did not occur by simply pressing the samples. The mechanochemical behavior in this study seems to be different from the mechanochemical conversion reaction from a polymeric to a monomeric form as observed for $[\text{VO}\{\text{sal}-(R,R)\text{-stien}\}]$ ($\text{H}_2\{\text{sal}-(R,R)\text{-stien}\} = N,N'$ -disalicylidene- (R,R) -1,2-diphenyl-1,2-ethanediamine) and $[\text{VO}(5\text{-Brsalen})]$ ($\text{H}_2(5\text{-Brsalen}) = N,N'$ -di-5-bromosalicylidene-1,2-ethanediamine) (**3,4**). In those cases, the color changed from orange to green, and the intensity of the $\text{V}=\text{O}$ stretching bands of the polymeric forms decreased with a complementary increase of those of the monomeric forms on grinding. For example, orange $[\text{VO}\{\text{sal}-(R,R)\text{-stien}\}]$ with a polymeric structure turned green on grinding, and the ground product showed the $\text{V}=\text{O}$ stretching band at 990 cm^{-1} in addition to the original 860 cm^{-1} absorption. However, only a decrease in intensity of the $\text{V}=\text{O}$ stretching band at 875 cm^{-1} was observed in the spectrum of **1g**. Although a new band which could be assignable to the $\text{V}=\text{O}$ stretching band of a monomeric form appeared at 996 cm^{-1} in the spectrum of **2g**, the intensity was very weak. The IR spectrum of **1gs** in a Nujol mull showed a strong $\text{V}=\text{O}$ stretching band at 867 cm^{-1} , indicating that a polymeric form was regenerated by suspending **1g** in acetonitrile. The spectrum of **1h** also showed a $\text{V}=\text{O}$ stretching band at 865 cm^{-1} .

The electronic spectra of **1**, **1gs**, and **2** show a $d-d$ transition band at 853, 867, and 752 nm, respectively (11). These spectra are similar to those of other polymeric Schiff base-oxovanadium(IV) complexes in the solid state (5,13). On the other hand, the spectra of **1g** and **2g** do not show the $d-d$ band clearly. The spectra of **1g** and **2g** which show gentle slopes in the region 550–1000 nm are different from those of polymeric or monomeric complexes (5).

The X-ray powder diffraction patterns (XRD) of **1**, **1g**, **1gs**, and **1h** are shown in Fig. 5. The XRD pattern of **1** shows several diffraction peaks in the range of 2θ (Cu $K\alpha$) = 5 to 40° . However, the pattern of **1g** does not show diffraction

peaks except for the traces of the peaks of **1**. This result indicates that crystalline **1** almost completely turned to an amorphous product **1g** on grinding. The diffraction pattern of **1gs** shows several diffraction peaks, and the pattern is similar to that of **1h**. It indicates that **1gs** and **1h** have similar crystal structures. The pattern of **2** shows several diffraction peaks in the range of 2θ (Cu $K\alpha$) = 5 to 40° , while that of **2g** does not show diffraction peaks except for the traces of the peaks of **2** (13).

Thermogravimetry (TG) measurements revealed that **1** and **1g** have two and one H_2O molecules of crystallization per vanadium atom, respectively (14). The decrease of the crystal water from two H_2O for **1** to one H_2O for **1g** indicates removal of weakly bound crystal water on grinding of **1**. On the other hand, TG measurements revealed that both **2** and **2g** have half an H_2O molecule of crystallization per vanadium atom. Removal of crystal water does not seem to occur on grinding of **2**. TG measurements of **1h** and **1gs** showed that they have $1H_2O$ and $0.5H_2O \cdot 0.2CH_3CN$ molecules of crystallization per vanadium atom, respectively. It seems that the water molecules of crystallization were incorporated into **1h** on leaving it to stand in the air after heating.

The temperature dependence of magnetic susceptibilities of the complexes in the temperature range 1.8 to 300 K is shown in Fig. 6. The magnetic data of **1** and **1gs** above 30 K follow the Curie-Weiss law, $\chi_m = C/(T - \theta)$, with Curie constants $C = 0.373$ and $0.348 \text{ emu K mol}^{-1}$ and Weiss constants $\theta = +7.5 \text{ K}$ and $+2.5 \text{ K}$, respectively. The magnetic data of **1g** also follow the Curie-Weiss law, but the Weiss constant was reduced compared to that of **1**. Almost identical $\chi_m T$ values at 300 K for **1** ($0.38 \text{ emu K mol}^{-1}$) and **1g** ($0.39 \text{ emu K mol}^{-1}$) corresponding the doublet spin centers ($0.375 \text{ emu K mol}^{-1}$ for $S = 1/2$ and $g = 2$) support that no oxidation occurred on grinding of **1**. Positive θ values indicate the ferromagnetic intermolecular interactions between the molecules in the chains of polymeric oxovanadium(IV) complexes (15). The temperature dependence of **1** and **1gs** was quantitatively interpreted in terms of the Heisenberg one-dimensional chain model (16) with coupling constants $J = +5.7 \text{ cm}^{-1}$ and $g = 1.99$ for **1** (15), and $J = +5.3 \text{ cm}^{-1}$ and $g = 1.83$ for **1gs**. The $\chi_m T$ value of **1** reached $1.03 \text{ emu K mol}^{-1}$ at 1.8 K. However, the $\chi_m T$ value of **1g** reached $0.55 \text{ emu K mol}^{-1}$ at 1.8 K. A smaller increase in the $\chi_m T$ value for **1g** than in that for **1** below 30 K indicates that magnetically noninteracting vanadium(IV) molecules were formed on grinding. The magnetic data of **2** and **2g** show magnetic properties similar to those of **1** and **1g**, respectively (17).

The spectroscopic and magnetic results discussed above suggest the following mechanism for the mechanochemical reaction of **1** and **2**. Grinding of **1** and **2** cleaves the $\dots V=O \dots V=O \dots$ bonds to yield various fragments of the polymeric chains. Amorphization of the crystals also

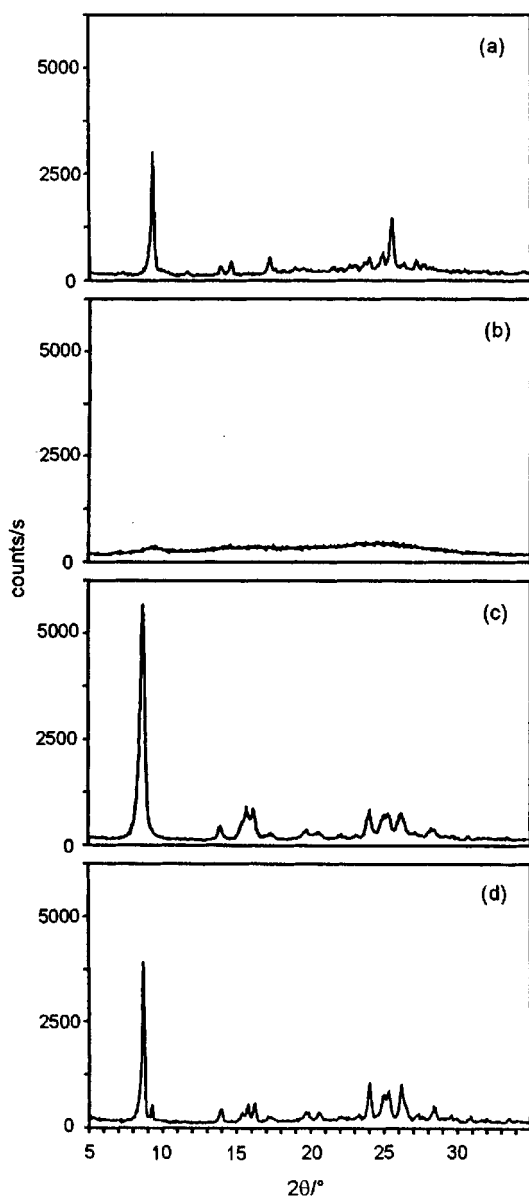


FIG. 5. XRD patterns of (a) **1**, (b) **1g**, (c) **1gs**, and (d) **1h** with Cu $K\alpha$.

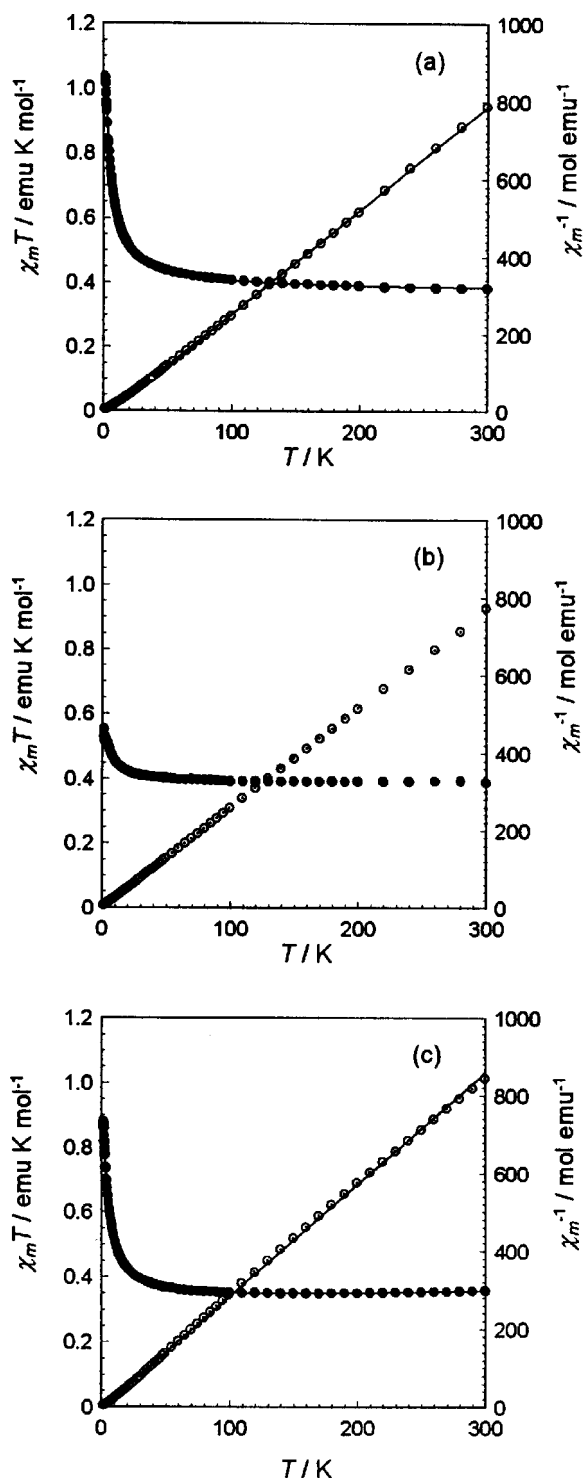


FIG. 6. $\chi_m^{-1}-T$ (○) and $\chi_m T-T$ (●) plots of (a) **1**, (b) **1g**, and (c) **1gs**.

occurs on grinding. The fragments produced on grinding of **1** and **2** will be inhomogeneous in their size and shapes, and have different V=O stretching frequencies. As there are so many species with different V=O stretching frequencies, the

V=O stretching bands of the ground complex **1g** will be too weak to be observed. The weak new band at 996 cm^{-1} in the IR spectrum of **2g** may be a V=O stretching band of the molecules which do not coordinate to the other molecules with their terminal oxygen atoms (molecules at the edges of the fragments or monomeric species). The IR spectra of more severely ground complexes with a ball-mill (**1g'** and **2g'**) show a small increase in intensity of the V=O stretching band at 992 cm^{-1} for **1g'** and 996 cm^{-1} for **2g'** (18). Hard grinding will produce smaller fragments of the polymeric chains.

The IR spectra of the polymeric oxovanadium(IV) complexes with Schiff base ligands derived from 5-nitrosalicylaldehyde and related diamines (1,2-propanediamine, 1,3-propanediamine, *rac*- and *meso*-1,2-cyclohexanediamine, etc.) in Nujol mulls showed a strong V=O stretching band at $867\text{--}877\text{ cm}^{-1}$. The intensity of the V=O stretching bands also significantly decreased when the IR spectra were measured in KBr disks. This result indicates that all the polymeric 5-NO₂-substituted complexes show a mechanochemical behavior similar to that of **1** and **2**. Polymeric Schiff base-oxovanadium(IV) complexes can be classified into three types from a mechanochemical point of view: (a) complexes such as [VO(saltn)] which do not show significant change on grinding; (b) 5-NO₂-substituted complexes such as **1** and **2** which yield fragments of polymeric chains; and (c) complexes like [VO{sal-(*R,R*)-stien}] and [VO(5-Brsalen)] which convert to a monomeric form on grinding (3, 4). The XRD patterns of the ground complexes of all of the three types show a significant decrease in the intensity of the diffraction peaks. The factors which control the mechanochemical behavior are unclear at present.

AUXILIARY MATERIAL

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