Bull. Chem. Soc. Jpn., 74, 2101–2105 (2001)

Synthesis and Crystal Structures of Polymeric and Dimeric Forms of an Oxotitanium(IV) Complex with a Tetradentate Schiff Base Ligand

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(Received May 8, 2001)

Polymeric and dimeric forms of an oxotitanium(IV) complex with a tetradentate Schiff base ligand, [TiO(salen)]·0.33CH_3OH (**1**) (H_2salen: *N*,*N*′-disalicylidene-1,2-ethanediamine) and [{TiO(salen)}$_2$]·2DMF (**2**), were prepared by the reaction of the Schiff base ligand with [{TiO(acac)$_2$}$_2$] (H_2acac: acetylacetone) in methanol and in DMF, respectively. X-ray crystal structure analyses of both complexes were carried out. Complex **1** has a linear ···Ti=O···Ti=O··· chain structure with the Ti=O and O···Ti distances being 1.705(2)–1.706(2) and 2.095(2)–2.134(2) Å, respectively. Complex **2** has a dimeric di-μ-oxo structure with the Ti–O distances being 1.804(2) and 1.907(2) Å. A strong band at 744 cm^{-1} in the IR spectrum of **1** was assigned unambiguously to the Ti=O stretching band by an ^{18}O-labelling experiment.

Oxotitanium(IV) complexes with tetradentate Schiff base ligands are known to have various structures in the solid state: dimeric μ-oxo structures (Ti–O–Ti);[1–3] dimeric di-μ-oxo structures;[4,5] trimeric (Ti=O···Ti–O–Ti) and tetrameric (Ti=O···Ti–O–Ti···O=Ti) structures;[3] and a chain structure that is formed by jointing the tetrameric units (Ti=O···Ti–O–Ti···O=Ti)$_n$.[3]

The preparation of Schiff base-oxotitanium(IV) complexes by the reaction of tetradentate Schiff base ligands with [{TiO(acac)$_2$}$_2$] (H_2acac: acetylacetone) in methanol was reported by Gullotti and Pasini.[6,7] They assigned the structure of the products as a polymeric linear ···Ti=O···Ti=O··· chain structure based on the IR spectra of the complexes. A band at 800–810 cm^{-1} was assigned as a Ti=O stretching band of the polymeric complex.[6,7] However, there is no evidence for the polymeric structure of the complexes based on X-ray crystal structure analyses, and the assignment of the Ti=O stretching band is uncertain. This paper reports on the preparation and crystal structures of the two forms of an oxotitanium(IV) complex, polymeric [TiO(salen)]·0.33CH_3OH (**1**) (H_2salen: *N*,*N*′-disalicylidene-1,2-ethanediamine) and dimeric di-μ-oxo [{TiO(salen)}$_2$]·2DMF (**2**). Complexes **1** and **2** were prepared by the reaction of the Schiff base ligand with [{TiO(acac)$_2$}$_2$] in methanol and in DMF, respectively. This is the first report of the crystal structure of the polymeric (···Ti=O···Ti=O···) oxotitanium(IV) complex. The ^{18}O-labelled oxotitanium(IV) complexes were also prepared in solutions containing $H_2{}^{18}O$, and the titanium-oxo vibration bands in the IR spectra were assigned. The structures of the complexes in solution were studied by ^1H NMR spectroscopy.

Results and Discussion

Crystals in two different forms of an oxotitanium(IV) complex with a Schiff base ligand, [TiO(salen)]·0.33CH_3OH (**1**) and [{TiO(salen)}$_2$]·2DMF (**2**), were prepared by the reaction of the Schiff base ligand with [{TiO(acac)$_2$}$_2$] in methanol and in DMF, respectively. Complex **1** was obtained by a method similar to that described in reference 6. However, another form of the oxotitanium(IV) complex, **2**, was obtained by the same reaction in DMF. Both **1** and **2** are yellow and only slightly soluble in organic solvents. However, **1** and **2** show rather different IR spectra (vide infra). Crystals suitable for X-ray crystal structure analyses were obtained by the reaction in dilute solutions.

X-ray crystal structure analyses of **1** and **2** were carried out. The molecular structures of **1** and **2** are shown in Figs. 1 and 2. Selected bond lengths and angles for **1** and **2** are listed in Tables 1 and 2, respectively. Complex **1** has a polymeric ···Ti=O···Ti=O··· structure. Three independent molecules in the unit cell have a distorted octahedral coordination geometry. Two linear chains that have a similar structure, ···Ti2–O7···Ti1–O4··· and ···Ti3–O10··· chains, run along the c axis in the crystal.[8] The Ti=O and Ti···O distances are 1.705(2)–1.706(2) and 2.095(2)–2.134(2) Å, respectively. The Ti=O···Ti angles are 166.7(1)–178.7(1)°. The Ti atoms are displaced by 0.195(1)–0.211(1) Å from the N_2O_2 coordination planes. All of the five-membered N–N chelate rings show a gauche conformation. The oxygen atom of methanol is hydrogen bonded to the O11 atom of the complex with the O···O distance being 2.793(4) Å. The Ti=O distances in polymeric **1** are rather longer than those in monomeric oxo(porphyrinato)titanium(IV) complexes with a square pyramidal structure (1.61–1.63 Å).[9–13] The structure of polymeric **1** is different from those of other polymeric oxometal complexes with ···M=O···M=O··· structures.[14–18] For example, the Ti=O distances are longer and the Ti···O distances are shorter than the V=O and V···O distances in polymeric [VO(salpn)] (H_2salpn: *N*,*N*′-disalicylidene-1,3-propanediamine), which has a linear ···V=O···V=O··· chain structure in the solid state (V=O distance: 1.633(9) Å, and V···O distance: 2.213(9) Å).[14] The double-bond character of the titanium–oxo bonds is decreased in

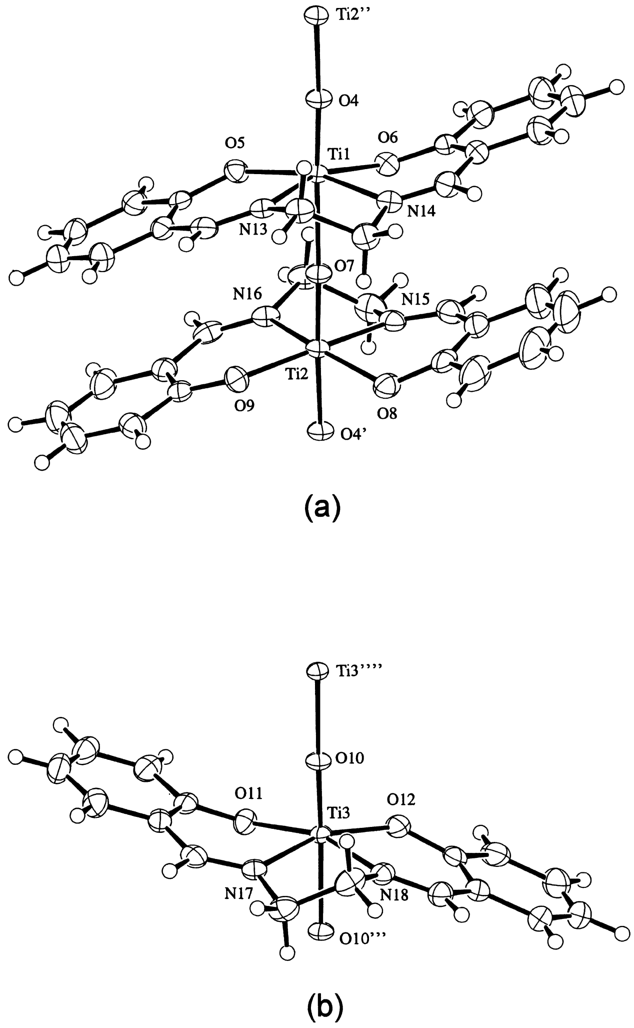

Fig. 1. ORTEP drawings of (a) ···Ti2–O7···Ti1–O4··· and (b) ···Ti3–O10··· chains in **1** with 40% probability ellipsoids, methanol molecule being omitted.

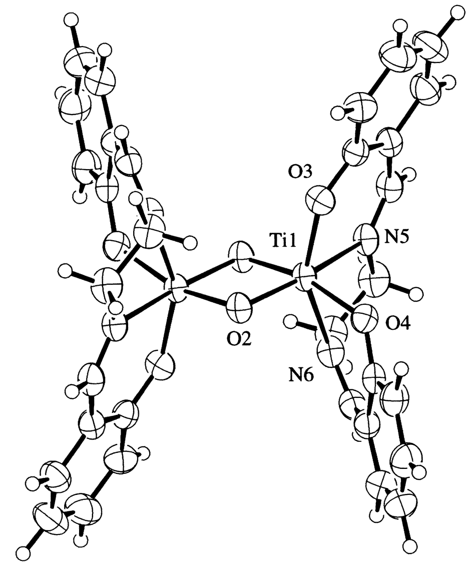

Fig. 2. ORTEP drawing of **2** with 40% probability ellipsoids, DMF molecules being omitted.

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

Ti1–O4	1.706(2)	Ti1–O5	1.915(2)
Ti1–O6	1.937(2)	Ti1–O7	2.126(2)
Ti1–N13	2.151(3)	Ti1–N14	2.156(3)
Ti2–O4′	2.134(2)	Ti2–O7	1.705(2)
Ti2–O8	1.940(2)	Ti2–O9	1.915(2)
Ti2–N15	2.159(3)	Ti2–N16	2.156(3)
O4–Ti1–O5	101.3(1)	O4–Ti1–O6	98.3(1)
O4–Ti1–O7	167.0(1)	O4–Ti1–N13	90.9(1)
O4–Ti1–N14	88.5(1)	O5–Ti1–O6	109.7(1)
O5–Ti1–N13	86.4(1)	O5–Ti1–N14	160.2(1)
O6–Ti1–N13	159.2(1)	O6–Ti1–N14	85.4(1)
N13–Ti1–N14	76.2(1)	O4′–Ti2–O7	166.5(1)
O7–Ti2–O8	98.6(1)	O7–Ti2–O9	101.3(1)
O7–Ti2–N15	89.1(1)	O7–Ti2–N16	91.8(1)
O8–Ti2–O9	109.8(1)	O8–Ti2–N15	84.9(1)
O8–Ti2–N16	158.3(1)	O9–Ti2–N15	160.1(1)
O9–Ti2–N16	86.4(1)	N15–Ti2–N16	76.3(1)
Ti1′–O4′–Ti2	166.7(1)	Ti1–O7–Ti2	167.4(1)
Ti3–O10	1.706(2)	Ti3–O10‴	2.095(2)
Ti3–O11	1.949(2)	Ti3–O12	1.916(2)
Ti3–N17	2.157(3)	Ti3–N18	2.151(3)
O10–Ti3–O10‴	168.24(4)	O10–Ti3–O11	96.8(1)
O10–Ti3–O12	101.2(1)	O10–Ti3–N17	88.9(1)
O10–Ti3–N18	92.4(1)	O11–Ti3–O12	109.9(1)
O11–Ti3–N17	85.5(1)	O11–Ti3–N18	159.4(1)
O12–Ti3–N17	160.0(1)	O12–Ti3–N18	86.1(1)
N17–Ti3–N18	76.2(1)	Ti3‴–O10‴–Ti3	178.7(1)

a) Primed and triple primed atoms are generated by x, y, $-1 + z$ and x, $1/2 - y$, $1/2 + z$, respectively.

polymeric **1**.

Complex **2** has a centrosymmetric dimeric di-μ-oxo structure. The two bridging oxo ligands are in the cis position. The salen ligand moiety has a non-planar folded geometry with the coordination of the O4 and N5 atoms in the trans position of the oxo ligands. The Ti–O (oxo) distances are 1.804(2) and 1.907(2) Å, which are longer than the Ti=O distances in **1**. The Ti–O–Ti angle is 98.20(9)°. Complex **2** has a highly distorted octahedral coordination geometry. The O3–Ti1–N6 angle is 151.1(1)°, and the Ti1–O4 (1.972(2) Å) and Ti1–N5 (2.251(3) Å) distances in the trans position of the oxo ligands are longer than the Ti1–O3 (1.887(2) Å) and Ti1–N6 (2.152(2) Å) distances. A strong trans influence of the oxo ligands affects the elongation of the titanium-ligand atom distances in the trans position of the oxo ligands.

The IR spectra of **1** and **2** are shown in Fig. 3. Polymeric complex **1** and dimeric complex **2** show rather different spectra. To assign the titanium–oxo vibration bands, ^{18}O-labelled oxotitanium(IV) complexes were prepared in methanol or in DMF containing $H_2{}^{18}O$. The spectrum of the ^{18}O-labelled **1** in Fig. 3b shows a new strong broad band at 711 cm^{-1} with a large decrease in intensity of the strong broad band at 744 cm^{-1} in the spectrum of **1** in Fig. 3a. On the other hand, the spectrum of the ^{18}O-labelled **2** in Fig. 3d shows a new band at

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

Ti1–O2	1.804(2)	Ti1–O2′	1.907(2)
Ti1–O3	1.887(2)	Ti1–O4	1.972(2)
Ti1–N5	2.251(2)	Ti1–N6	2.152(2)
O2–Ti1–O2′	81.80(9)	O2–Ti1–O3	105.72(9)
O2–Ti1–O4	92.54(9)	O2–Ti1–N5	163.2(1)
O2–Ti1–N6	102.5(1)	O2′–Ti1–O3	102.46(8)
O2′–Ti1–O4	165.43(9)	O2′–Ti1–N5	82.26(9)
O2′–Ti1–N6	87.75(9)	O3–Ti1–O4	91.98(9)
O3–Ti1–N5	82.77(9)	O3–Ti1–N6	151.1(1)
O4–Ti1–N5	101.71(9)	O4–Ti1–N6	80.34(9)
N5–Ti1–N6	71.73(9)	Ti1–O2–Ti1′	98.20(9)

a) Primed atoms are generated by $1 - x, -y, 2 - z$.

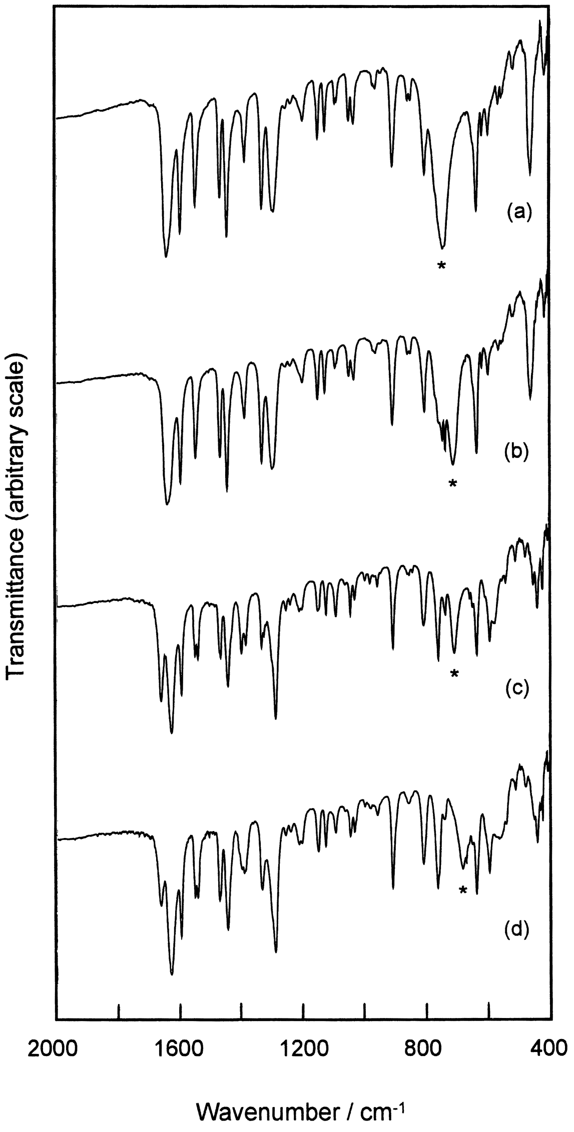

Fig. 3. IR spectra of (a) **1**, (b) ^{18}O-labelled **1**, (c) **2**, (d) ^{18}O-labelled **2** in KBr disks. The titanium-oxo vibration bands are shown in the figures with asterisks.

681 cm^{-1} with a large decrease in intensity of the band at 709 cm^{-1} in the spectrum of **2** in Fig. 3c. Thus, the strong broad band at 744 cm^{-1} in the spectrum of **1** is assigned to the Ti=O stretching band. The band at 709 cm^{-1} in the spectrum of **2** is assigned to the Ti–O–Ti asymmetric stretching band.[19] The assignment of the Ti=O stretching band in references 6 and 7 is not correct. The band at 800–810 cm^{-1}, which had been reported as a Ti=O stretching band by Gullotti and Pasini,[6,7] must be a vibration band of the Schiff base ligand. The Ti=O stretching band of **1** is largely shifted to lower energy than those of monomeric oxo(porphyrinato)titanium(IV) complexes (945–984 cm^{-1}).[9] It has not been reported that the Ti=O stretching band was observed at such a low frequency. The Ti=O stretching band of **1** at very low frequency can also be assigned as the Ti=O···Ti asymmetric stretching band.

In this study, polymeric complex **1** and dimeric complex **2** were obtained by the reaction of the Schiff base ligand with [{TiO(acac)$_2$}$_2$] in methanol and in DMF, respectively. To investigate the solvent effect, the preparation of the oxotitanium(IV) complexes was carried out by the reaction in other solvents, such as $CHCl_3$, CH_2Cl_2, CH_3CN, and DMSO. The structures of the products were assigned based on the IR spectra. The dimeric di-μ-oxo complex was obtained by the reaction in $CHCl_3$, in CH_2Cl_2, and in CH_3CN. The polymeric linear chain complex was obtained by the reaction in DMSO.[20] Measurements of the ^{1}H NMR spectra of **1** and **2** in dilute $CDCl_3$, DMSO-d^6, and CD_3OD solutions were carried out to determine the structures of the complexes in solution. Complexes **1** and **2** show a similar ^{1}H NMR spectrum in the same solvent. However, the spectra show a clear solvent dependence. The spectrum of **1** or **2** in $CDCl_3$ shows equivalent proton signals of the two salicylaldehyde moieties at δ = 8.21–6.81 and two methylene proton signals at δ = 3.94 and 3.30. This indicates that the oxotitanium(IV) complex is monomeric and has C_s symmetry in $CDCl_3$. On the other hand, the spectrum of **1** or **2** in DMSO-d^6 shows non-equivalent proton signals of the two salicylaldehyde moieties, which indicates that the oxotitanium(IV) complex has a monomeric structure with C_1 symmetry or a dimeric di-μ-oxo structure in DMSO-d^6. The spectrum of **1** or **2** in CD_3OD shows complicated multiplet peaks in the regions δ = 6.5–9.0 and 3.7–4.5, which indicates that more than two species exist in the solution. This solvent dependence was not reported in a previous NMR study of dimeric di-μ-oxo oxotitanium(IV) complexes with optically-active Schiff base ligands.[4] Although it is difficult to elucidate the relation between the structures of the complex in each solution and those in the crystals, the formation of the polymeric or dimeric structure in the crystals may be due to the solubility of the two forms in each solution at equilibrium.

Experimental

[TiO(salen)]·0.33CH$_3$OH (1). [{TiO(acac)$_2$}$_2$] (1.31 g, 2.5 mmol) and the ligand H$_2$salen (1.35 g, 5 mmol) were added to 50 cm^3 of methanol. The reaction mixture was stirred for one day at room temperature to yield a light-yellow precipitate. It was collected by filtration, and washed with methanol and ether. Yield: 0.44 g (26%). Found: C, 57.29; H, 4.24; N, 8.24%. Calcd for $C_{16.33}H_{15.33}N_2O_{3.33}Ti_1$: C, 57.56; H, 4.53; N, 8.22%. ^{1}H NMR ($CDCl_3$) δ 8.21 (s, 1H, N=CH), 7.38 (dd, J = 8.8, 7.3 Hz, 1H, Ph), 7.28 (d, $J = 7.3$ Hz, 1H, Ph), 6.92 (d, $J = 8.8$ Hz, 1H, Ph), 6.81 (dd, $J = 7.3, 7.3$ Hz, 1H, Ph), 3.94 (dd, $J = 11.7, 6.3$ Hz, 1H, CH_2), 3.30 (dd, $J = 11.7, 6.3$ Hz, 1H, CH_2). ^{1}H NMR (DMSO-d^6) δ 8.65 (s, 1H, N=CH), 8.52 (s, 1H, N=CH), 7.53 (d, $J = 7.3$ Hz, 1H, Ph), 7.51 (d, $J = 7.3$ Hz, 1H, Ph), 7.43 (dd, $J = 8.3, 7.3$ Hz, 1H, Ph), 7.41 (dd, $J = 8.3, 7.3$ Hz, 1H, Ph), 6.85 (dd, $J = 7.3, 7.3$ Hz, 1H, Ph), 6.84 (d, $J = 8.3$ Hz, 1H, Ph), 6.77 (dd, $J = 7.3, 7.3$ Hz, 1H, Ph), 6.65 (d, $J = 8.3$ Hz, 1H, Ph), 4.26 (dd, $J = 12.7, 6.8$ Hz, 1H, CH_2), 3.88 (m, 2H, CH_2).

[{TiO (salen)}$_2$]·2DMF (2). Complex **2** was prepared by the reaction of the Schiff base ligand with [{TiO(acac)$_2$}$_2$] in DMF. All other reaction conditions were similar to those for **1**. The resulting light-yellow precipitate was collected by filtration and washed with DMF and ether. Yield: 1.7 g (87%). Found: C, 56.68; H, 5.23; N, 10.38%. Calcd for $C_{38}H_{42}N_6O_8Ti_2$: C, 56.59; H, 5.25; N, 10.42%.

Preparation of the ^{18}O-Labelled Oxotitanium(IV) Complexes. 0.1 cm^3 (ca. 5 mmol) portions of $H_2{}^{18}O$ (95 > atom%) were added to 10 cm^3 of dry methanol and dry DMF. [{TiO(acac)$_2$}$_2$] (0.0131 g, 0.025 mmol) and the ligand H$_2$salen (0.0135 g, 0.05 mmol) were added to the solutions and the mixtures were stirred under an argon atmosphere for one day. The resulting precipitates were collected by filtration, and washed with ether and dried.

Crystal Structure Determination. Prismatic crystals of **1** and plate crystals of **2** were prepared by the reaction in dilute solutions. [{TiO(acac)$_2$}$_2$] (0.131 g, 0.25 mmol) and the ligand H$_2$salen (0.135 g, 0.5 mmol) were added to 150 cm^3 of methanol and DMF. The mixtures were stirred for ca. one hour and filtered. The yellow filtrates were left standing for ca. one week at room temperature to yield yellow crystals of **1** and **2**. The intensity data were collected at 25 °C on a Rigaku four-circle AFC-7R diffractometer with graphite-monochromatized Mo-$K\alpha$ radiation (λ = 0.71073 Å) up to $2\theta = 55°$ by ω scans for **1**, and $\theta{-}2\theta$ scans for **2**. Three standard reflections were measured at every 150 reflections. Absorption corrections were made by the numerical integration method for **1**,[21] and the Ψ scans method for **2**.[22] The structures were solved by direct methods on a Silicon Graphics O^2 workstation with the program system TEXSAN,[23] and refined with SHELXL-97.[24] Non-hydrogen atoms were treated anisotropically, and hydrogen atoms attached to the carbon atoms were introduced at ideal positions. The hydrogen atom attached to the oxygen atom in **1** was located from difference synthesis, and refined isotropically. The refinement was based on F^2 against all 10438 reflections for **1**, and against 4478 reflections for **2**. The R value was 0.047 for the 5645 reflections with $I > 2\sigma(I)$ for **1**, and 0.050 for 3025 reflections with $I > 2\sigma(I)$ for **2**. The crystal data and experimental details are listed in Table 3. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC 158029 and 158030. The complete data are deposited as Document No. 74053 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 3. Crystallographic Data for **1** and **2**

	1	**2**
Chem formula	$C_{16.33}H_{15.33}N_2O_{3.33}Ti_1$	$C_{38}H_{42}N_6O_8Ti_2$
Fw	340.78	806.58
Crystal size/mm	0.20 × 0.15 × 0.15	0.70 × 0.15 × 0.05
Space group	$Pbca$	$P\bar{1}$
a/Å	36.887(5)	10.278(1)
b/Å	32.652(8)	13.246(2)
c/Å	7.5614(6)	7.630(1)
α/°	90	101.92(1)
β/°	90	97.57(1)
γ/°	90	102.493(9)
V/Å^3	9107(4)	975.2(2)
Z	24	1
ρ_{calc}/g cm^{-3}	1.491	1.373
μ/cm^{-1}	5.81	4.68
λ/Å	0.71073	0.71073
Temp/°C	25	25
$R^{a)}$ ($I > 2\sigma(I)$)	0.047	0.050
$R_w{}^{b)}$	0.145	0.146

a) $R = \Sigma |F_o{}^2 - F_c{}^2| / \Sigma F_o{}^2$.
b) $R_w = [\Sigma w (F_o{}^2 - F_c{}^2)^2 / \Sigma w (F_o{}^2)^2]^{1/2}$,
$w^{-1} = \sigma^2 (F_o{}^2) + (0.0609P)^2 + 1.8468P$ for **1**, and
$w^{-1} = \sigma^2 (F_o{}^2) + (0.0790P)^2 + 0.2314P$ for **2**, where
$P = (F_o{}^2 + 2F_c{}^2)/3$.

Other Measurements. The IR spectra were recorded on a JASCO A-202 spectrophotometer. The ^{1}H NMR spectra were recorded on a JEOL JNM- GX400 spectrometer with TMS reference.

The author thanks Prof. Masaaki Kojima (Okayama University) for valuable discussions. The present work was supported in part by the Moritani Scholarship Foundation.

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