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Syntheses and Characterizations of Cyclotitanosiloxane and Cyclozirconosiloxane Compounds

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The syntheses and characterizations of cyclotitanosiloxane (CTS) and cyclozirconosiloxane (CZS) were investigated. CTS and CZS were synthesized by the reaction of di-*t*-butoxysilanediol with bis(acetylacetonato)diisopropoxidotitanium(IV) or bis(acetylacetonato)diisopropoxidozirconium(IV) in benzene. The formation of CTS and CZS was confirmed by the NMR and IR spectra and elemental analysis. The X-ray structural analysis for single crystals revealed that CTS and CZS consist of an eight-membered ring of two titano- or zirconosiloxane linkages bearing two *t*-butoxy groups on a silicon atom and two acetylacetonato groups on a titanium or zirconium atom.

Polymetallosiloxane is a promising compound as a precursor polymer for ceramic materials because it consists of a metallosiloxane bond in the main chain which is easily converted to oxide ceramic materials. We have been interested in the preparation of oxide ceramic materials by a precursor method via the polymetallosiloxanes, by which SiO_2–M_xO_y ceramic fibers, thin films, bulk bodies, and fine powders were prepared by the reaction of silicic acid or partially hydrolyzed tetraethoxysilane with a metal chelate compound, alkoxide, or chloride.[1—8] The polymetallosiloxanes are, however, random copolymers of siloxane domain and metalloxane domain, because it is difficult to control the microstructure of polymetallosiloxanes by conventional synthetic techniques.

In this paper we report on the preparation of cyclotitanosiloxane and cyclozirconosiloxane compounds together with detailed X-ray analytical data according to Scheme 1, which are suitable for the formation of polymetallosiloxanes with a controlled microstructure as a precursor for ceramic materials. In relation to this work, we have reported on the preparation and characterization of titanosiloxane and zirconosiloxane compounds by the reaction of di-*t*-butoxymethoxysilanol with tetraisopropoxidotitanium(IV) or tetraisopropoxidozirconium(IV), and the reaction of di-*t*-butoxymethoxysilanol with bis(acetylacetonato)diisopropoxidotitanium(IV) or bis(acetylacetonato)diisopropoxidozirconium(IV)[9] with the aim of forming polymetallosiloxane by the selective hydrolysis of the methoxy group, which is more hydrolyzable than the *t*-butoxy group. In addition, we have briefly reported on the formation of cyclotitanosiloxane (CTS) by the reaction of di-*t*-butoxysilanediol with bis(acetylacetonato)diisopropoxidotitanium(IV) as a monomer for the ring-opening polymerization; however, no detail characterization has been carried out for CTS.[4]

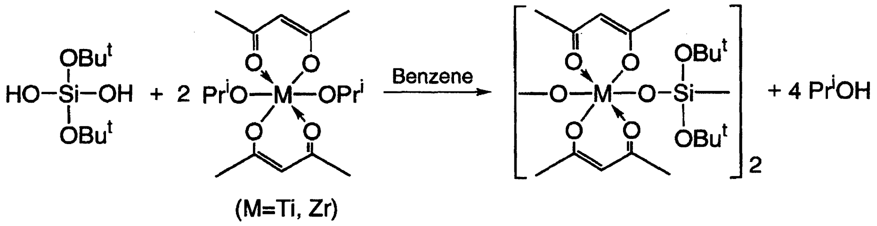
Results and Discussion

Synthesis of Cyclotitanosiloxane (CTS). Table 1 shows the results of the synthesis of CTS. The progress of the reaction was monitored by the determination of the alcohols by gas chromatography (GC). In Runs 1, 2 and 3, isopropyl alcohol was recovered almost quantatively to result in the formation of CTS in 90% yield, of which gel permeation chromatography (GPC) showed a single peak. In Runs 4, 5, and 6, on the other hand, the amount of isopropyl alcohol formed

Table 1. Reaction Conditions and Yield of CTS[a)]

Run	Temperature	Time	Yields (%)		
	°C	h	Pr^iOH[b)]	Bu^tOH[b)]	CTS[c)]
1	50	1	83	0	86
2	50	4	86	0	86
3	50	8	75	0	86
4	80	1	81	0	86
5	80	4	48	35	39
6	80	8	44	48	32

a) Reaction scale: DSD; 2.08 g (0.01 mol), PTP; 3.64 g (0.01 mol), Benzene (20 ml). b) Determined by GC. c) Isolation yield by reprecipitation.



Scheme 1.

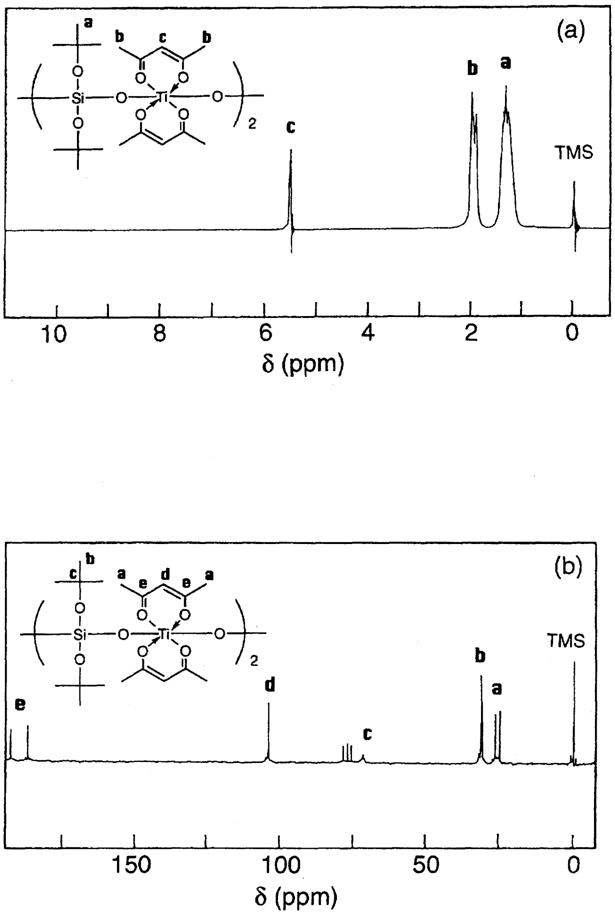


Fig. 1. ^{1}H and ^{13}C NMR spectra of CTS in chloroform-*d*.

decreased while that of *t*-butyl alcohol increased as the reaction proceeded. With an increase of *t*-butyl alcohol, the isolation yield of CTS decreased in addition to the appearance of several peaks in GPC in Runs 5 and 6. Under the conditions of Runs 4, 5 and 6, *t*-butoxy groups should be eliminated to produce polymeric titanosiloxane compounds. As a result, Run 1 was prefered as being best for the synthesis of CTS. CTS showed no melting point, but a decomposition point and an appreciable stability to hydrolysis compared with titanium tetraisopropoxide. CTS was easily soluble in alcohols, THF, chloroform, carbon tetrachloride, and benzene, but less soluble in hexane. The structure of CTS was identified by NMR and IR spectra, and metal analysis: The ^{1}H, ^{13}C, and ^{29}Si NMR spectra showed signals with reasonable chemical shifts. The IR spectrum indicated absorption peaks due to acac, Bu^{t}O–, and Si–O–Ti linkages. Metal analysis also showed good agreement with the calculated values. The analytical data support the structure of CTS.

In the ^{1}H NMR spectrum of CTS, shown in Fig. 1(a), the signals due to the Bu^{t}O– group and a methyl group in the acac group split into three and two singals, respectively. In addition, the ^{13}C NMR spectrum of CTS (Fig. 1(b)), showed two pairs of doublets due to CH$_3$– and $\rangle$C=O carbons in the acac group. These spectral data indicate that the free rotation of Bu^{t}O– is restricted because of a steric hindrance of the methyl group in the acac group. The methyl group in the acac group is very close to the methyl group in the Bu^{t}O– group, and thus increases the repulsion of hydrogen atoms, which results in unequal magnetic fields of two methyl groups in an acac group to split the signals due to the Bu^{t}O– and acac groups.

The crystal structure of CTS and crystal data are shown in Fig. 2 and Table 2. A unit cell contains one molecule of CTS and two molecules of benzene. CTS consists of one eight-membered ring of two Si–O–Ti–O linkages bearing Bu^{t}O– groups on a silicon atom and acac groups on a titanium atom as pendants. The bond lengths of Si–O and Ti–O in an eight-membered ring were about 1.62 and 1.80 Å, respectively, which are almost identical compared to the mean bond lengths of Si–O and Ti–O linkages. The bond angles of two Si–O–Ti linkages were 172° and 154°, which suggests that the eight-membered ring is almost a plane with bent bonds of Si–O–Ti. Silicon and titanium atoms have sp^3 and d^{2}sp^3 orbitals to form tetrahedral and octahedral configurations, respectively. The acac groups attached to the titanium atom are in the *cis* configuration, which is also suggested by the ^{1}H and ^{13}C NMR spectra. The bond angle of the O–Ti–O linkage in the acac groups attached to a titanium atom were 82.9° and 82.3°, which are smaller than the angle expected from the octahedral configuration, 90°. The dihedral angle of two acac groups is 80.6°, indicating that two acac groups on a titanium atom are arranged in a *cis* configuration, but are not perpendicular to each other.

Synthesis of Cyclozirconosiloxane (CZS). Table 3 shows the results of the synthesis of CZS. The progress in the reaction was monitored by a determination of the alcohols produced by a GC analysis. In Runs 1, 2, and 3, isopropyl alcohol was recovered quantatively to result in the formation of CZS in 90% yield, of which the GPC showed a single peak. In Runs 4 to 9,

Table 2. Crystal Data and Structure Refinement for CTS and CZS

Compound	CTS	CZS
Empirical formula	$C_{48}H_{76}O_{16}Si_2Ti_2$	$C_{37}H_{65}Cl_3O_{16}Si_2Zr_2$
Crystal color, habit	Transparent, plate	Transparent, block
Crystal size/mm	0.40×0.35×0.10	0.50×0.35×0.20
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*P*2(1)/*n*
Unit cell dimensions *a*/Å	10.8389(7)	12.991(2)
b/Å	12.6730(11)	17.653(2)
c/Å	12.7696(8)	22.134(2)
α/°	103.445(7)	90
β/°	110.477(5)	95.798(10)
γ/°	111.403(5)	90
Volume/Å^3	1396.4(2)	5050.0(11)
Peaks to determine cell	54	45
q range of cell peaks/°	10.0 to 27.5	5.6 to 25.0
Temperature/K	113(2)	196(2)
Wavelentgh/Å	1.54178	0.71073
Z	1	4
Formula weight	1061.07	1110.86
Density (calculated)/Mg m^{-3}	1.265	1.461
Absorption coefficient/mm^{-1}	3.371	0.680
F(000)	564	2296
Relfections collected	7238	13703
Independent reflections	3619	6590
R value	0.0373	0.0564

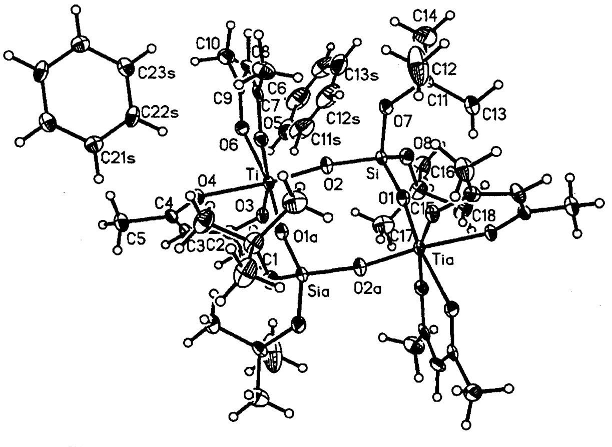


Fig. 2. X-Ray analytical structure of CTS.

on the other hand, the amount of isopropyl alcohol decreased while that of *t*-butyl alcohol increased as the reaction proceeded. With the increase of *t*-butyl alcohol, the isolation yield of CZS decreased in addition to the appearance of several peaks in GPC. Under the conditions of Runs 4 to 9, *t*-butoxy groups are replaced with isopropoxy groups to produce polymeric zirconosiloxane compounds. Thus, Run 1 was prefered as being best for the synthesis of CZS. CZS showed no melting point, but a decomposition point and an appreciable stability to hydrolysis compared with zirconium tetraisopropoxide. CZS was easily soluble in alcohols, THF, chloroform, carbon tetrachloride, and benzene, but less soluble in hexane. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra showed signals due to the Bu^{t}O– group and acac groups. The IR spectrum of CZS showed absorption peaks due to Si–O–Zr–O– bonds and an acac group. Metal analysis also showed good agreement with the calculated values. These analytical data supports the structure of CZS.

In the ^{1}H and ^{13}C NMR spectra of CZS (shown in Fig. 3(a) and 3(b)), the signals due to the methyl groups in the Bu^{t}O– and acac groups were observed in two singlets. The free rotation of the Bu^{t}O– group is not restricted in CZS, which may arise from a longer atomic radius of the zirconium atom than the titanium atom to allow a larger space in CZS than in CTS.

Table 3 and Fig. 4 show the results on a structural analysis of the CZS single crystal. The crystal form is monoclinic, which comprises four CZS molecules and four chloroform molecules in a unit cell. CZS consists

Table 3. Reaction Conditions and Yield of CZS[a)]

Run	Temperature	Time	Yields (%)		
	°C	h	Pr^{i}OH[b)]	Bu^{t}OH[b)]	CZS[c)]
1	30	1	87	0	91
2	30	4	87	0	94
3	30	8	87	0	92
4	50	1	92	8	96
5	50	4	87	22	92
6	50	8	82	27	87
7	80	1	61	45	83
8	80	4	52	56	55
9	80	8	34	60	12

a) Reaction scale: DSD; 2.08 g (0.01 mol), PZP; 4.08 g (0.01 mol), Benzene (20 ml). b) Determined by GC. c) Isolation yield by reprecipitation.

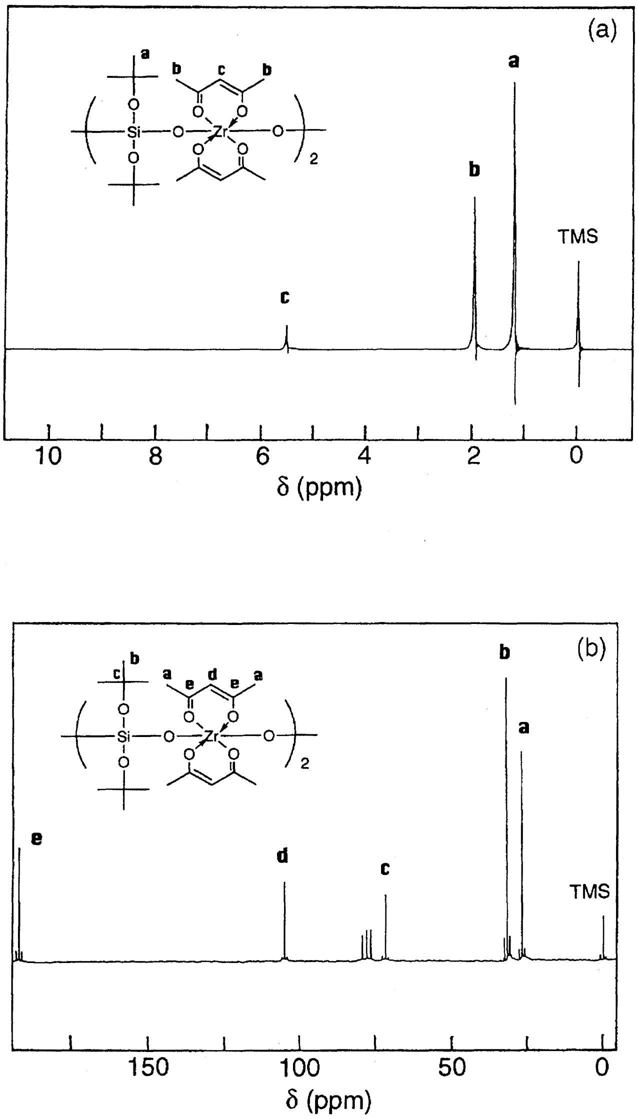


Fig. 3. ^{1}H and ^{13}C NMR spectra of CZS in chloroform-*d*.

of one eight-membered ring of two Si–O–Zr–O linkages bearing Bu^{t}O– groups on a silicon atom and acac groups on a zirconium atom as pendants, where the acac groups are arranged into a *cis* configuration. The oxygen atom in an eight-membered ring is located closer to the silicon atom than the zirconium atom. The bond lengths of Si–O and Zr–O in an eight-membered ring were about 1.61 and 2.10 Å, respectively, which are almost identical with the mean bond lengths of the Si–O and Zr–O bonds. The bond angles of four Si–O–Zr were 165, 158, 170, and 157°, which suggests that the eight-membered ring does not consist of a plane, but a slightly bent plane. Silicon and zirconium atoms have sp^3 and d^{2}sp^3 orbitals to form tetrahedral and octahedral configurations, respectively. The acac groups attached to the zirconium atom are arranged in *cis*. The bond angles of the O–Zr–O bonds in two acac groups attached to the zirconium atom were 77.8° and 79.0°, which are smaller than the angle expected from the octahedral configuration, 90°. The dihedral angle of two acac groups is 78.0°, indicating that acac groups on a zirconium atom are arranged *cis*, but not perpendicular, to each other.

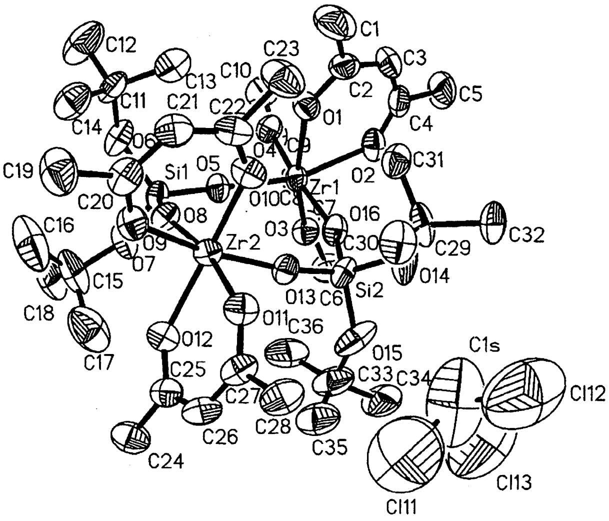


Fig. 4. X-Ray analytical structure of CZS.

Experimental

Materials. All experiments were carried out under a nitrogen atmosphere. Di-*t*-butoxysilanediol ((Bu^{t}O)$_2$Si(OH)$_2$, DSD),[10] bis(acetylacetonato)diisopropoxidotitanium(IV) ((acac)$_2$Ti(OPr^i)$_2$, PTP), and bis(acetylacetonato)diisopropoxidozirconium(IV) ((acac)$_2$Zr(OPr^i)$_2$, PZP) were synthesized according to the literature.[11,12]

Syntheses of Cyclotitanosiloxane (CTS, 2,2,6,6-Tetra-*t*-butoxy-4,4,8,8-tetrakis(2,4-pentanedionato-κ^2*O*)-2,6-disila-4,8-dititana-1,3,5,7-tetraoxacyclooctane). A solution of PTP (3.64 g, 0.01 mol) in 10 ml of benzene was added to a solution of DSD (2.08 g, 0.01 mol), followed by heating at 50 °C for 1 h. The solvents were removed under reduced pressure followed by reprecipitation: CTS was dissolved in 10 ml of benzene and poured into 150 ml of hexane with vigorous stirring, followed by filtration to give a yellowish-white powder. A single crystal of CTS was isolated by a solvent-evaporation method; CTS was dissolved in benzene and stored at room temperature to gradually evaporate the solvent for several days.[13] Yield, 85%. Mp, 188—192 °C (Decomposition). ^{1}H NMR δ=1.3 (9H, t, –OBu^t), 2.0 (6H, d, C–CH$_3$), 5.5 (1H, s, –CH=). ^{13}C NMR δ=25.3 (CH$_3$CO–), 26.8 (CH$_3$CO–), 31.6 ((CH$_3$)$_3$CO–), 71.7 ((CH$_3$)$_3$CO–), 103.8 (–CH=), 185.9 (CH$_3$CO–), 191.8 (CH$_3$CO–). ^{29}Si NMR δ=−107.8. IR 1590 ($\nu_{\mathrm{C=O}}$), 1530 ($\nu_{\mathrm{C=C}}$), 1000 ($\nu_{\mathrm{Si–O–C}}$), 960 cm^{-1} ($\nu_{\mathrm{Si–O–Ti}}$). Found: Si, 6.1; Ti, 10.5%. Calcd for $\mathrm{C_{36}H_{64}O_{16}Si_2Ti_2}$: Si, 6.2; Ti, 10.6%.

Syntheses of Cyclozirconosiloxane (CZS, 2,2,6,6-Tetra-*t*-butoxy-4,4,8,8-tetrakis(2,4-pentanedionato-κ^2*O*)-2,6-disila-4,8-dizircona-1,3,5,7-tetraoxacyclooctane). A solution of PZP (4.08 g, 0.01 mol) in 10 ml of benzene was added to a solution of DSD (2.08 g, 0.01 mol) followed by heating at 30 °C for 1 h. The solvents were removed under reduced pressure followed by reprecipitation; CZS was dissolved in 10 ml of benzen and poured into 150 ml of hexane with vigorous stirring followed by filtration to give a yellowish-white powder. A single crystal was isolated by a solvent-evaporation method; CZS was dissolved in chloroform and stored at room temperature to gradually evaporate solvent for several days.[13] Yield, 97%. Mp, 197—198 °C (Decomposition). ^{1}H NMR δ=1.3 (9H, s, –O**Bu**^{t}), 2.0 (6H, s, C–$\mathbf{CH_3}$), 5.6 (1H, s, –**CH**=). ^{13}C NMR δ=26.5 ($\mathbf{CH_3}$CO–), 31.5 (($\mathbf{CH_3}$)$_3$CO–), 71.0 ((CH$_3$)$_3$**C**O–), 104.0 (–**C**H=), 190.8 (CH$_3$**C**O–). ^{29}Si NMR δ=−102.3. IR 1590 ($\nu_{C=O}$), 1530 ($\nu_{C=C}$), 1010 (ν_{Si-O-C}), 970 ($\nu_{Si-O-Zr}$). Found: Si, 5.6; Zr, 18.4%. Calcd for $C_{36}H_{64}O_{16}Si_2Zr$: Si, 5.7; Zr, 18.4%.

Instruments and Analysis. ^{1}H NMR spectra were measured using a JEOL PMX60SI spectrometer in chloroform-*d*. ^{13}C NMR spectra were measured using JEOL FX-90Q spectrometer in chloroform-*d* with a complete decoupling method at the resonance frequency of 22.53 MHz. ^{29}Si NMR spectra were measured using a JEOL FX-90Q spectrometer in chloroform-*d* by a non-decoupling method at the resonance frequency of 17.80 MHz. IR spectra were measured using a Hitachi 260-50 IR spectrophotometer by a carbon tetrachloride solution method. GC was measured using Ohkura GC-103; Column: SE-30 (2 m). GPC were measured using Nihon Seimitsu Kagaku HPLC system; Column: Tosoh HLX3000 and Shodex A-801; Eluent: THF; Detector: Nihon Bunseki Kogyo RI detector. X-Ray structural analysis was carried out at University of Wisconsin-Madison. A metal analysis was carried out by the following process. At first, 0.2 g of the sample was weighed in a crucible and 0.5 ml of sulfuric acid was added followed by heating and weighing the residue (A). Second, 0.2 g of the sample was weighed in a flask and heated in the presence of 1 g of ammonium sulfate, 1 g of ammonium nitrate, and 20 ml of sulfuric acid. The residue was poured into 100 g of ice followed by filtration. The filtrate was subjected to firing in a crucible followed by weighing (B). The content of SiO_2 was calculated from content (B) and the content of TiO_2 or ZrO_2 was calculated from the difference between contents (A) and (B).

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