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Preparation, Optical Resolution, Racemization, and Ligand Isotopic Exchange of Tris(1,3-diphenyl-1,3-propanedionato)germanium(IV) Perchlorate in Acetonitrile

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Tris(1,3-diphenyl-1,3-propanedionato)germanium(IV) $[Ge(bzbz)_3]^+$ was prepared as crystalline perchlorate, and resolved by the crystallization of its salt with hydrogen (*R,R*)-*O,O*-dibenzoyltartrate. The patterns of UV and circular dichroism spectra are very similar to those of $[Si(bzbz)_3]ClO_4$. The racemization of the Δ-$[Ge(bzbz)_3]ClO_4$ was studied kinetically in acetonitrile at 40—60 °C to find the rate law: Rate$=k_{rac}$[complex], where $k_{rac}=9.86\times10^{-5}\ s^{-1}$ at 50 °C. The activation parameters ($\Delta H^{\ast}=99\pm2$ kJ mol^{-1} and $\Delta S^{\ast}=-17\pm2$ J K^{-1} mol^{-1}) are very similar to those of tris(acetylacetonato)germanium(IV) complex. Compared with the rate of ligand isotopic exchange, the racemization should proceed *via* intramolecular mechanism. The steric effect coming from the substituents on the chelate ring should play an important role in determining the racemization rate.

We had studied the kinetics of racemization and ligand isotopic exchange of tris(acetylacetonato)germanium(IV) $[Ge(acac)_3]^+$.[1,2] With aims of understanding the detailed processes of the intramolecular racemization of tris(β-diketonato)germanium(IV) complex, our study has been extended to tris(1,3-diphenyl-1,3-propanedionato)germanium(IV) $[Ge(bzbz)_3]^+$. The pK_a value (K_a; acid dissociation constant) of 1,3-diphenyl-1,3-propanedione (Hbzbz) is greater by ten times than that of acetylacetone, and different electronic and steric effects are expected. This paper deals with the synthesis, the resolution and the kinetics of racemization in acetonitrile of this new complex.

Experimental

Materials. *Preparation of* $[Ge(bzbz)_3]ClO_4$ *and* $[Ge(bzbz)_3]Cl$: $[Ge(acac)_3]ClO_4$ was synthesized by the reported procedure.[1] An acetonitrile solution (80 cm^3) of $[Ge(acac)_3]ClO_4$ (2.8 g, 6.0×10^{-3} mol) and Hbzbz (14.8 g, 6.6×10^{-2} mol) was refluxed with stirring at *ca.* 110 °C for *ca.* 120 h, and poured into diethyl ether (500 cm^3). The yellow precipitates were filtered off and recrystallized from acetonitrile by adding diethyl ether. Pale-yellow needles melted at 289 °C with decomposition, and are soluble in acetonitrile, chloroform, acetone, nitromethane and glacial acetic acid. Found: C, 64.10; H, 4.21; Ge (as GeO_2 in ash), 8.85%. Calcd for $C_{45}H_{33}O_{10}ClGe$: C, 64.19; H, 3.95; Ge, 8.62%. The UV absorption spectra in acetonitrile are shown in Fig. 1. The IR absorption pattern in KBr disc is very similar to that of $[Si(bzbz)_3]ClO_4$. ^{1}H-NMR spectra in CD_3CN show phenyl peaks at 8.1—8.2(*ortho*), 7.65(*meta*), 7.5(*para*) ppm and a methine peak at 7.75 ppm *vs.* tetramethylsilane (TMS).

$[Ge(bzbz)_3]Cl$ was prepared by treating $[Ge(bzbz)_3]ClO_4$ with the anion exchange resin Amberlyst A-26 (Cl^--type) in acetonitrile, and crystallized by adding diethyl ether.

Optical Resolution: $[Ge(bzbz)_3]Cl$ (320 mg, 8.5×10^{-4} mol) was dissolved in 56 cm^3 of acetonitrile-acetone (5 : 2), and treated with sodium hydrogen (*R,R*)-*O,O*-dibenzoyltartrate (340 mg, 8.5×10^{-4} mol) in 24 cm^3 of aqueous acetone (5 : 1). Two hundred cm^3 of water was dripped to the solution at a rate of 3 cm^3 per minute with stirring at room temperature to give oily precipitates, which were recrystallized from acetonitrile by adding diethyl ether. A solution of this diastereoisomer (0.8 g, 7.2×10^{-4} mol) and magnesium perchlorate (1.0 g, 4.5×10^{-3} mol) in 60 cm^3 of glacial acetic acid was poured into diethyl ether to give partially resolved, optically active $[Ge(bzbz)_3]ClO_4$, which was collected by filtration. The product was fractionally crystallized from chloroform solution by adding diethyl ether. (yield *ca.* 10%) Circular dichroism spectrum of the partially resolved complex is shown in Fig. 1. (The optical resolution seems to be *ca.* 6% in this case.)

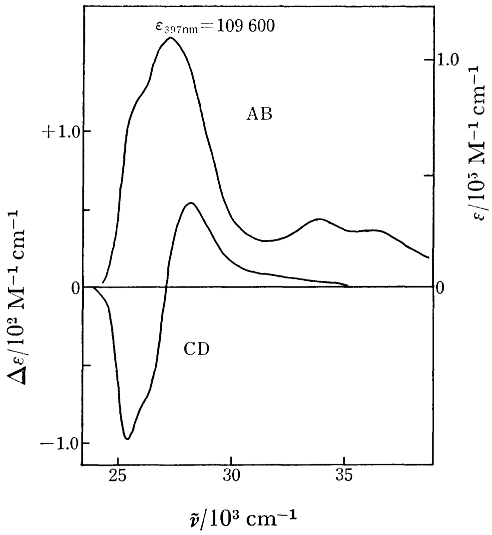

Fig. 1. Ultraviolet absorption (AB) and circular dichroism (CD) spectra of $(-)_{589}$-$[Ge(bzbz)_3]ClO_4$ in acetonitrile.

Other Reagents: Acetonitrile, trichloroacetic acid, pyridine, and tetraethylammonium perchlorate were purified by the ordinary methods. The labelled Hbzbz(Hbzbz[^{14}*C*]) was prepared by the Claisen condensation between ethyl benzoate[^{14}*C*] and acetophenone, and purified by recrystallization from ethanol (specific radioactivity; 19.1 mCi/g).

Kinetic Procedure. *Racemization*: Acetonitrile solution containing the optically active $[Ge(bzbz)_3]ClO_4$, and other reagents whenever necessary, was kept in a thermostatted cell at 40 to 60 °C (±0.1 °C), and the progress of racemization was followed by observing the CD strength at a proper wavelength in the range from 390 to 414 nm. The UV spectra of the reaction mixtures were also recorded before and after the kinetic runs. The water content in the complex solution was determined by Karl Fischer titration.

Isotopic Exchange: The complex and Hbzbz[^{14}C] were dissolved in acetonitrile. Aliquots were sealed in pyrex-glass tubes and placed in a thermostat (60 and 90 °C). The ampoules were chilled one by one at proper time intervals, and the contents were poured into cold diethyl ether. Precipitated [Ge(bzbz)$_3$]ClO$_4$ was filtered off, dried *in vacuo*, and dissolved in acetonitrile. The solution was divided into two portions. One portion was mixed with *p*-bis(5-phenyl-2-oxazolyl)benzene(POPOP) solution in toluene and the β-activity was counted with a liquid scintillation counter. Another portion was diluted with acetonitrile and the extinction was measured at 377 nm to find the concentration of the complex. The rate of isotopic exchange was calculated on the basis of the change of specific activities of the complex by McKay's formula.[5)]

Apparatus. Hitachi 323 Spectrophotometer and JASCO model J-40 Spectropolarimeter were used for recording the UV absorption and CD spectra respectively. The β-activity of ^{14}C was recorded with a Nuclear Chicago Unilux II-A Liquid Scintillation Counter.

Results

The Kinetics of Racemization in Acetonitrile. The logarithm of CD strength decreased linearly with the reaction time. The extinction of UV spectra remained unchanged during several half-lives, and the decrease in CD strength should be due to intrinsic racemization of the complex. The rate was proportional to the complex concentration (5×10^{-6} to 5×10^{-3}M) (Fig. 2), and expressed by the rate law

$$\text{Rate} = k_{\text{obsd}}[\text{complex}] = 2k_{\text{rac}}[\text{complex}]. \qquad (1)$$

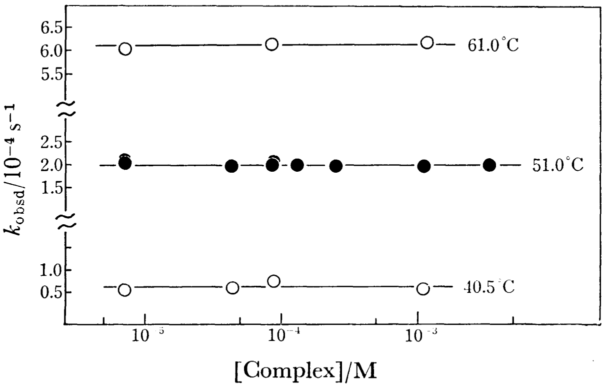

Fig. 2. Influence of the complex concentration upon k_{obsd} in acetonitrile.

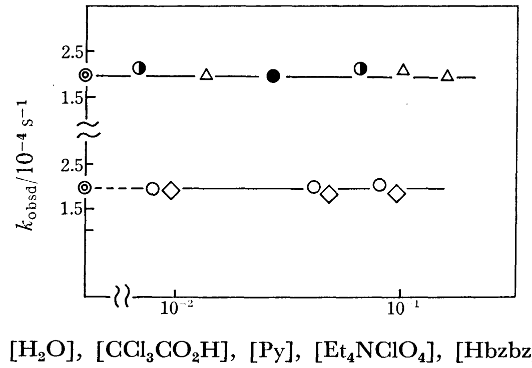

Fig. 3. Influence of water, acid, pyridine, free ligand, and tetraethylammonium perchlorate concentration upon the racemization rate in acetonitrile at 51 °C. △: Water, ◇: trichloroacetic acid, ○: pyridine, ●: dibenzoylmethane, ◑: tetraethylammonium perchlorate, and ◎: without any reagent.

Water (10^{-3} to 10^{-1}M) gave no influence on the racemization rate. (Fig. 3.) Neither did free Hbzbz, trichloroacetic acid, and pyridine in the concentration ranges given in Fig. 3. The rate is insensitive to the ionic strength ($<6.5\times10^{-2}$ mol dm^{-3} by tetraethylammonium perchlorate.) The rate constants and activation parameters are shown in Table 1.

Ligand Isotopic Exchange. Experimental conditions were as follow: [Ge(bzbz)$_3$ClO$_4$]$=3.95\times10^{-3}$ M, [Hbzbz-^{14}C]$=4.97\times10^{-2}$ M, [H$_2$O]$=3.17\times10^{-2}$ M. No exchange was observed at 60 °C within 1500 min. However, at 90 °C, the ligand exchange was observed and the following rate law was obtained.

$$\text{Rate} = k_{\text{obsd}}[\text{complex}],\ k_{\text{obsd}} = 2.18\times10^{-8}\,\text{s}^{-1} \qquad (2)$$

Discussion

Bond Rupture Mechanism. The results are summarized in Table 1 together with those of the related complexes. The [Ge(bzbz)$_3$]$^+$ racemizes faster but exchanges the ligand slower than [Ge(acac)$_3$]$^+$ does. Absence of solvolysis, hydrolysis and ligand isotopic exchange at 40 to 60 °C under the given conditions indicates that the racemization proceeds *via* an intramolecular mechanism. Absence of influence of the concentrations of the complex and the free ligand on the rate also supports this mechanism. The rate

TABLE 1. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE RACEMIZATION AND THE LIGAND ISOTOPIC EXCHANGE IN ACETONITRILE

Complex[a)]	pK_a of ligand[b)]	k_1(50 °C) / 10^{-5} s^{-1}	ΔH^* / kJ mol^{-1}	ΔS^* / J K^{-1} mol^{-1}	k_2 / s^{-1}	k_{ex}(90 °C) / s^{-1}
[Ge(acac)$_3$]$^+$	11.8	2.88	102±2	−18±6	2.7×10^{-4}	6.48×10^{-6} [c)]
[Ge(bzbz)$_3$]$^+$	13.4	9.86	99±2	−17±2	0[d)]	2.18×10^{-8}
[Si(acac)$_3$]$^+$	11.8	3.87	108±1	+2	1.5×10^{-1}	Not observed within 10 h at 50 or 60 °C
[Si(bzbz)$_3$]$^+$	13.4 (9.70)[e)]	5.46	105±4	−4	0[d)]	
[Si(meacac)$_3$]$^+$	(11.8)[e)]	180	117±4	+59	3.0×10^{-2}	

Racemization rate: $R=(k_1+k_2[\text{base}])[\text{complex}]$, Ligand isotopic exchange rate: $R=k_{\text{ex}}[\text{complex}]$

a) Counter anion is ClO$_4^-$ in all cases. b) In CH$_3$OH, from Ref. 4. c) Calculated from activation parameters in Ref. 2, and [H$_2$O]$=3\times10^{-2}$ M. d) Pyridine has no catalitic action in this case. e) In 50% aqueous dioxan, Ref. 6.

was not influenced by water, trichloroacetic acid, pyridine and tetraethylammonium perchlorate. These facts might appear to be consistent with the twist mechanism without bond break throughout the racemization. However, we tend to think that the present racemization proceeds *via* bond break mechanism, by comparing the activation parameters with those of related compounds. Racemization of $[Ge(acac)_3]^+$ was claimed to involve a solvent assisted break of Ge–O bond, on the basis of solvent effect (*i.e.* linear correlation between the racemization rate and the nucleophilicity of the solvents[1]). The ΔH^* and ΔS^* values of the present racemization are very similar to those for the $[Ge(acac)_3]^+$ complex.

Jones and Fay studied the geometrical isomerization of dihalobis(β-diketonato)germanium(IV) in an equimolar mixture of diphenylmethane and 1,3-dimethoxybenzene by the nmr line broadening technique and proposed an intramolecular mechanism involving the break of one Ge–O bond. The activation enthalpy and entropy are respectively 103 ± 6 kJ mol^{-1}, -5 ± 13 J mol^{-1} K^{-1} for $[GeCl_2(dpm)_2]$ (dpm; enolate anion of 2,2,6,6-tetramethyl-3,5-heptanedione). These values are also very similar to ours, and provide support to the postulation that the racemization involves one Ge–O bond break as rate determining step.

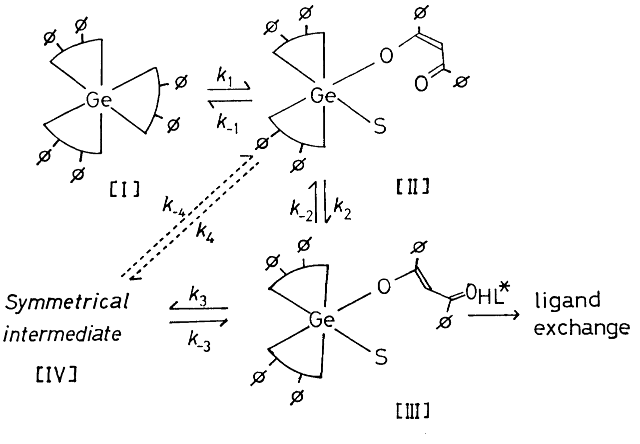

Fig. 4. Racemization mechanism of $[Ge(bzbz)_3]^+$ in acetonitrile.
S; Solvent molecule (acetonitrile). The present kinetics was studied only in acetonitrile because of the solubility, and the role of solvent molecules was not examined. From the analogy to the racemization mechanism of $[Ge(acac)_3]^+$, however, the vacant coordination site formed by the break of one Ge–O bond is likely to be occupied by an acetonitrile molecule (donor number 14.1).[8] HL*; labelled Hbzbz.

$[Ge(bzbz)_3]^+$ with a more basic ligand racemizes faster than $[Ge(acac)_3]^+$. If the racemization rate were governed by the ease of bond break alone, the rate should depend directly on the pK_a of the free ligand. Hence, some other factors must be encountered. The proposed mechanism is visualized in Fig. 4. We studied the racemization kinetics of some tris (β-diketonato)silicon(IV) complexes[3], and found that the $[Si(meacac)_3]^+$(meacac; enolate anion of 3-methyl-2,4-pentanedione)racemizes faster in acetonitrile than $[Si(acac)_3]^+$ does, despite of the larger pK_a of Hmeacac than Hacac. This observation was interpreted by Eq. 3 by considering a mechanism similar to Fig. 4.

$$k_{\mathrm{rac}} = k_1 \frac{k_2}{k_{-1}+k_2} \frac{k_3}{k_{-2}+k_3}, \tag{3}$$

where k_1, k_{-1}, k_2, k_{-2}, and k_3 are the rates of Si–O bond break, ring closure, isomerizations of the unidentate ligand (from *cis* to *trans* and *vice versa*) and twist around Si(IV) respectively. The branching ratio $k_2k_3/(k_{-1}+k_2)(k_{-2}+k_3)$ for the meacac complex was considered to be greater than that for the acac complex on the basis of large steric interaction among the methyl groups in the state coresponding to II. A similar interpretation would be applicable to the present racemization, if the branching ratio were greater for the bzbz complex than for the acac complex. This assumption does not seem inadequate because molecular model studies disclose that more repulsive interaction is expected in II around the methine proton for the bzbz complex than for acac complex. However, there remains a possibility that the symmetrical transition state (IV) might be formed directly from II, so that the branching ratio is modified to $k_4/(k_4+k_{-1})$. Nevertheless a steric factor coming from the terminal group must be responsible for the faster racemization of $[Ge(bzbz)_3]^+$ than $[Ge(acac)_3]^+$.

On the other hand, the ligand isotopic exchange of $[Ge(bzbz)_3]^+$ is slower by *ca.* 300 times than of $[Ge(acac)_3]^+$ at 90 °C. On the basis of the ΔS^* value and the deuterium isotopic effect,[2] the isotopic exchange was claimed to be mostly governed by the ease of proton transfer from Hacac* to acac$^-$ in an intermediate of the form $[Ge(O,O\text{-acac})_2(O\text{-acac})(O\text{-acac}^*\,H)]^+$. If this mechanism commonly operates in the ligand isotopic exchange of $[Ge(bzbz)_3]^+$, increase in bulkiness of the terminal groups in the ligand will decrease the ease of proton transfer to result in slower isotopic exchange.

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