January, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(1), 131—135 (1974) 131

Optical Resolution and Racemization of Tris(acetylacetonato)-germanium(IV) in Organic Solvents

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(Received September 28, 1973)

The tris(acetylacetonato)germanium(IV) has been resolved by the crystallization of its hydrogen-*R*,*R*-dibenzoyltartrate in a mixture of acetonitrile, ethanol, and water. The racemization kinetics of perchlorate of the Δ-enantiomer has been studied in 1,1,2,2-tetrachloroethane (TCE), nitromethane, acetonitrile (AN), and *N*,*N*-dimethylformamide, the activation enthalpies ($\Delta H^{\neq}$/kcal·mol^{-1}) and the activation entropies ($\Delta S^{\neq}$/cal·K^{-1} mol^{-1}) being 27.9, 26.6, 24.3, and 23.3, and +3.7, −1.1, −4.4, and −5.0, respectively. The ligand isotopic exchange is much slower than the racemization under similar conditions. Consideration of acid (in TCE) and base (in AN) catalysis, influence of ionic strength and solvent effect suggests an intra-molecular mechanism *via* an intermediate in which one of the ligands is in unidentate state.

The number of work concerning germanium compounds has been increasing in these decades. However, most of them are related to tetrahedral organometallic compounds, and much less to octahedral and co-ordination compounds. Especially, the dynamic properties of six co-ordinated germanium complexes are almost unknown.[1–3]

Geometrical isomerization and racemization of octahedral complexes with tris-bidentate ligands have been studied by many workers with β-diketonato complexes of various metal ions. Most of these reactions in organic solvents are claimed to proceed *via* intra-molecular mechanism.[4] These works centered around chargeless complexes, and those related to univalent cationic complexes are limited to tris(acetylacetonato)-silicon(IV).[5]

We intended to extend the work to those with germanium(IV) analogues. Morgan and Drew[6] first prepared the tris(acetylacetonato)germanium(IV) ion, [Ge(acac)$_3$]$^+$, and its physical properties are better known than others. We have resolved this complex and studied the racemization kinetics in various organic solvents. The mechanism has been discussed and the lability of this complex compared with those of related compounds.

Experimental

Materials. Preparation of Tris(acetylacetonato)germanium(IV) Perchlorate: The complex ion [Ge(acac)$_3$]$^+$ was synthesized as hexachloroantimonate by Cox and co-workers' method.[7] This salt (3.5 g, 5×10^{-3}mol) was dissolved in 30 ml of chloroform–ethanol (3: 1), and mixed with silver perchlorate (1.25 g, 6×10^{-3}mol) in 20 ml chloroform–ethanol (1: 1). Silver chloride was filtered off, and the filtrate was treated with magnesium perchlorate (1.3 g) in 20 ml of chloroform–ethanol (1: 3). Crystals of [Ge(acac)$_3$]ClO$_4$ obtained on addition of diethyl ether (450 ml) were filtered off, washed with ether, recrystallized from chloroform solution by adding diethyl ether, washed with diethyl ether, and dried *in vacuo*. Yield, 80—87%. Found: C, 38.45; H, 4.64%. Calcd for $C_{15}H_{21}O_{10}ClGe$: C, 38.38; H, 4.51%. Colorless needles melt at 245—251 °C with decomposition. IR spectra in KBr disk and Nujol mull gave the absorption peaks of carbonyl group co-ordinated to metal ions, perchlorate anion, but not of hydroxyl groups. Proton NMR in deuterochloroform has singlet signals at 2.33 and 6.18 ppm (δ, TMS), corresponding to six methyls and one methyne, respectively. Figure 1 shows the UV absorption spectrum in acetonitrile. The pattern and the peaks agree with those of [Ge(acac)$_3$]$^+$ in [Ge(acac)$_3$][FeCl$_4$].

Optical Resolution: The complex ion was resolved into optical isomers by the crystallization of its hydrogen-*R*,*R*-dibenzoyltartrate. Racemic perchlorate (1.6 g, 3.4×10^{-3} mol) was dissolved in 75 ml of acetonitrile–ethanol–water (1: 1: 1), treated with 20 ml of sodium hydrogen dibenzoyltartrate (5.3×10^{-3}mol) in water, the mixture was poured into 130 ml of cold water, and set aside in an ice bath. The colorless needles were filtered off within 30 minutes and dried. The product was recrystallized from acetonitrile–ethanol (1: 1) solution by adding twice volume of water, filtered off and dried *in vacuo*. Found: C, 54.31; H, 4.53%. Calcd for $C_{33}H_{34}O_{14}Ge$: C, 54.40; H, 4.71%. mp 141—143 °C (decompn.). $[\alpha]_{589}$ −656 ° (4.4×10^{-4}M in AN, 20 °C).

This diastereoisomer (1.0 g, 1.4×10^{-3}mol) and magnesium perchlorate (1.0 g, 4.5×10^{-3}mol) were dissolved in 60 ml of

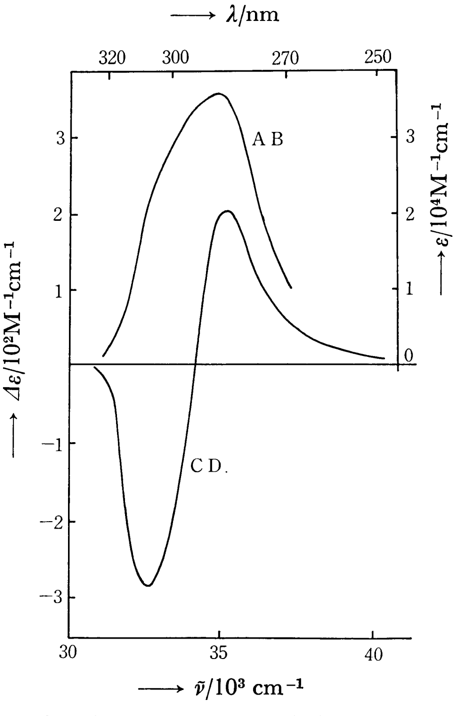

Fig. 1. Ultraviolet absorption (AB) and circular dichroism (CD) spectrum of (−)$_{589}$-[Ge(acac)$_3$]$^+$ in acetonitrile.

glacial acetic acid, and poured into diethyl ether. The crystals were washed with diethyl ether, recrystallized from chloroform solution with diethyl ether, and dried. The yield was 20% on the basis of racemic perchlorate. Found: C, 38.50; H, 4.63%. Calcd for $C_{15}H_{21}O_{10}ClGe$: C, 38.38; H, 4.51%. $[\alpha]_{589}$ $-930°$ (3.2×10^{-4}M in AN, 20 °C). Circular dichroism (CD) spectrum of the complex is shown in Fig. 1.

Solvents for Kinetic Runs: Acetonitrile (AN) was dried with calcium chloride, refluxed with diphosphorus pentoxide and distilled. This procedure was repeated and the middle fraction was finally distilled. Nitromethane was washed successively with aqueous sodium bicarbonate, sodium bisulfite, 5% sulfuric acid and water. One fourth volume of water was added and refluxed. The mixture was distilled slowly, a large amount of the first fraction was discarded and the oily layer of the middle fraction was again distilled. 1,1,2,2-Tetrachloroethane (TCE) was shaken with several portions of concentrated sulfuric acid until the acid remained colorless, and distilled under reduced pressure. Chloroform was washed with aqueous sodium hydroxide, sulfuric acid and water, and distilled. *N,N*-Dimethylformamide (DMF) was dried with anhydrous copper sulfate and distilled under reduced pressure. Dimethyl sulfoxide (DMSO) was dried with activated alumina and distilled under reduced pressure.

The purities of these solvents were checked by gas chromatography, and the water contents titrated by Karl Fischer method.

Other Reagents: Pyridine was recrystallized as perchlorate and dissolved in a small amount of water, treated with solid sodium hydroxide, the pyridine layer decanted and distilled under reduced pressure. Glacial acetic acid was frozen at 5 °C and distilled. Commercially available extra pure sodium perchlorate and magnesium perchlorate were used without purification. Acetylacetone (Hacac) was distilled by the usual method. The labelled acetylacetone (Hacac-^{14}C) was prepared as reported in the literature.[8)]

Kinetic Procedure. *Racemization*: The optically active perchlorate (0.01 g) was dissolved in a given solvent (25 ml) and, whenever necessary, other reagents were mixed. Aliquots of the solution were sealed in small glass test tubes with silicone rubber stoppers. All these procedures were operated in a dry grove box. Several ampoules were prepared, placed in a thermostat (30 to 70 °C$\pm$0.1 °C) and picked up one by one at proper intervals. They were cooled in ice water for 30 s, and their optical rotation and UV absorption were measured at room temperature (15—25 °C) at a proper wavelength in the range 310 to 365 nm. (AN, 310—325 nm; chloroform, 316 nm; TCE, DMF, and DMSO, 318 nm; nitromethane, 360—365 nm). The rate constant was calculated by the following equation,

$$k_{\mathrm{obsd}} = (1/2t)\ln(\alpha_0/\alpha_t) \qquad (1)$$

where α_0 and α_t are the optical rotation at time zero and t, respectively, and t is the lapse of time in second.

Isotopic Exchange: The complex and acetylacetone-^{14}C (10^{-3} M) were dissolved in acetonitrile. Aliquots were sealed in glass tubes, and kept in a thermostat (60 to 80 °C). They were chilled one by one at proper time intervals, the ampoules cut and poured into cold diethyl ether. The precipitated complex was filtered off with a piece of filter paper, washed with diethyl ether, and dried *in vacuo*. The activity of a weighed amount of crystals was counted with a 2π gas flow counter in a current of Q-gas.

Apparatuses. JASCO model ORD/UV-5 was used for the measurement of optical rotation and the recording of CD spectra. JASCO DIP-SL Polarimeter was used for optical rotation measurement at Na-D line. Hitachi 323 Spectrophotometer was used for the recording of absorption spectra, and K53 Gas Chromatograph with TCD for detecting the impurity of the solvents. Aloka FC-1E Counter was used for the β-activity counting of ^{14}C. The water content was measured by the Karl Fischer method. Metrohm E 365 B Konduktoskop and EA 608 bright platinum electrodes were used for the conductance measurement.

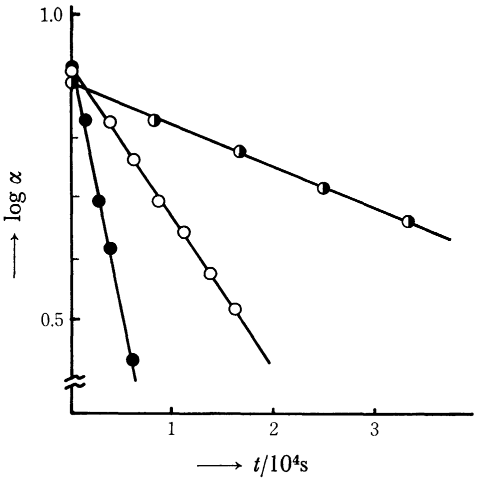

Fig. 2. Change in optical rotation at 312 nm in acetonitrile.
◑ 40 °C, ○ 50 °C, ● 60 °C

Results

The Kinetics of Racemization in Acetonitrile. The changes in optical rotation at 312 nm are illustrated in Fig. 2. The absorbances at 305 and 288 nm showed no change during several half-lives, and the decrease in optical rotation should be due to net racemization of the complex. The rate constant was found to be independent of the complex concentration. Hence the rate formula is expressed as follows:

$$\mathrm{Rate} = k_{\mathrm{obsd}}[\mathrm{complex}] \qquad (2)$$

The water content of the solution gave no significant effect on the racemization rate in the range from 10^{-2} to 2×10^{-1} M. (Fig. 3). Free acetylacetone (Hacac) and acetic acid gave no catalytic effect on the racemiza-

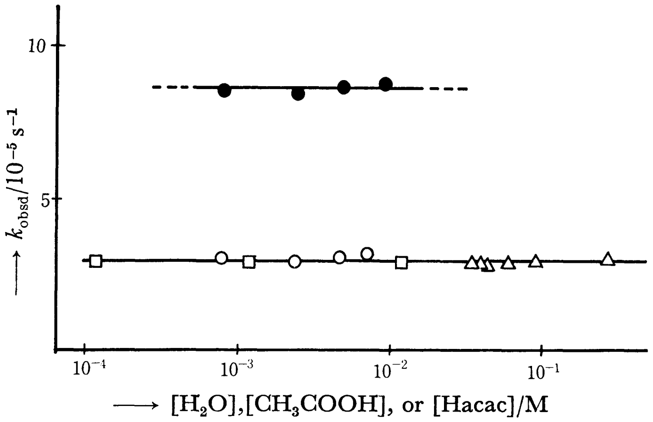

Fig. 3. Influence of water, acid, and ligand concentration upon the racemization rate in acetonitrile.
△ for water at 50 °C, ○ and ● for acetic acid at 50 and 60 °C, respectively, □ for Hacac at 50 °C.

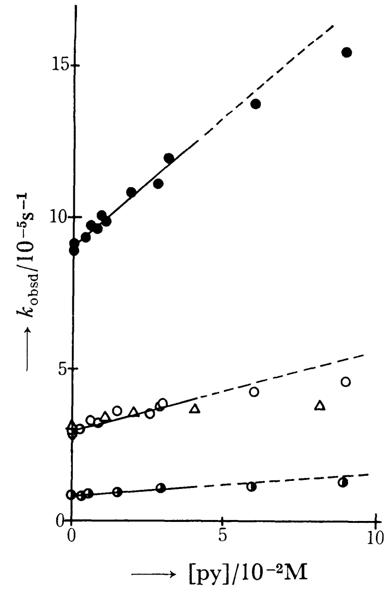

Fig. 4. Influence of pyridine concentration in acetonitrile.
Circles in the absence of $NaClO_4$, ◑ 40 °C, ○ 50 °C, ● 60 °C; △ in 0.124 M $NaClO_4$ at 50 °C.

tion rate (Fig. 3) in the ranges from 10^{-5} to 10^{-2} M and from 5×10^{-4} to 10^{-2} M, respectively.

The relationship between pyridine concentration and racemization rate is illustrated in Fig. 4. The diagrams are linear at least up to 4×10^{-2} M of pyridine. The intercepts coincide with the k_{obsd} values in the absence of pyridine. Hence the k_{obsd} is expressed by

$$k_{obsd} = k_1 + k_2[py] \qquad (3)$$

The values of k_1 and k_2 at several temperatures and the activation parameters are shown in Table 1.

The values of k_1 and k_2 depend on the concentration of sodium perchlorate. Conductance measurements suggested that sodium perchlorate is a strong, while the complex is a weak electrolyte in AN. Hence the increase in k_{obsd} with the electrolyte concentration seems to be due to ionic strength effect (see Fig. 5).

When the water content was increased to 1 M, UV absorption changes, but no isosbestic point was observed. The decrease in absorbance at 316 nm was in accord with the first-order kinetic formula at 70 °C and the apparent rate constant linearly increases with increase in water concentration up to 8 M. It seems that such a change is due to hydrolysis of the complex, presumably taking place step by step. The rate is so small, ($1\times10^{-4}/M^{-1}\,s^{-1}$ at 70 °C), however, that it can be ignored when the racemization mechanism is discussed.

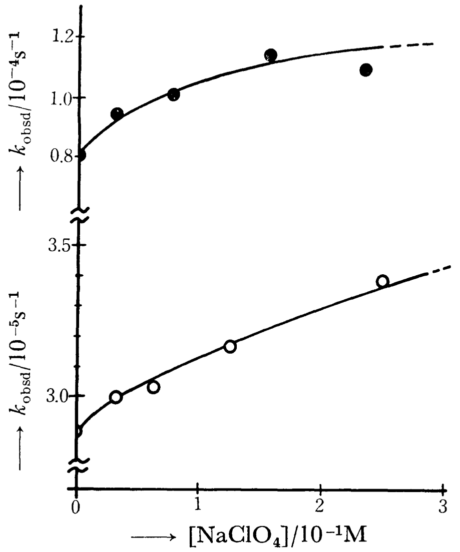

Fig. 5. Salt effect on the racemization rate in acetonitrile.
○ 50 °C, ● 60 °C.

Racemization in Other Solvents. No change in absorption of the complex was observed for several half-lives in nitromethane, and for a few half-lives in TCE. The racemization was catalyzed by acetic acid in TCE. The decrease in optical rotation in DMF was accompanied by the change in absorption. The absorption spectrum has an isosbestic point at 279 nm, and this change seems to be due to a reaction giving free acetylacetone. The net racemization was followed by use of the quotient (optical rotation at 316 nm)/(absorbance at 305 nm), and the calculated k_{obsd} values are shown in Table 2. The decrease in optical activity in DMSO and chloroform is mostly due to decomposition of the complex. Intrinsic racemization may be taking place, but it is distinguished with difficulty. The k_{obsd} values and the activation parameters in various solvents are summarized in Table 2.

Ligand Isotopic Exchange in Acetonitrile. No exchange took place within 2000 minutes at 60 °C both in the presence and the absence of pyridine. No exchange was either observed at 80 °C suggesting a negligibly smaller rate of ligand isotopic exchange than the racemization.

TABLE 1. RATE CONSTANTS AND ACTIVATION PARAMETERS IN ACETONITRILE

t/°C	$[Ge(acac)_3]^+$		$[Si(acac)_3]^{+\,5)}$	
	$k_1/10^{-5}s^{-1}$	$k_2/10^{-4}M^{-1}s^{-1}$	$k_1/10^{-5}s^{-1}$	$k_2/10^{-4}M^{-1}s^{-1}$
30	—	—	0.263	1.5
40	0.797	0.85	1.08	—
50	2.88	2.7	3.87	—
60	8.85	8.7	13.7	—
$\Delta H^{\ne}$/kcal·mol^{-1}	24.3±0.4	23.7±3.0	25.7±0.2	—
$\Delta S^{\ne}$/cal·K^{-1}·mol^{-1}	−4.4±1.4	−1.7±9.9	+0.5	—

TABLE 2. RACEMIZATION RATE CONSTANTS AND ACTIVATION PARAMETERS OF $[Ge(acac)_3]^+$ IN VARIOUS ORGANIC SOLVENTS

Solvent	1,1,2,2-Tetra-chloroethane	Nitromethane	Acetonitrile	*N*,*N*-Dimethyl-formamide
$k_{323}/10^{-5}s^{-1}$ a)	0.579	0.420	2.88	10.4
$k_{298}/10^{-7}s^{-1}$ b)	1.39	1.17	11.0	44
$\Delta H^{\ddagger}$/kcal·mol^{-1}	27.9±0.8	26.6±1.0	24.3±0.4	23.3±2.6
$\Delta S^{\ddagger}$/cal· K^{-1}· mol^{-1}	+3.8±2.8	−1.1±3.5	−4.4±1.4	−5.0±8.6
ε c)	8.20	35.9	37.5	36.7
$\mu/10^{-18}$ CGSesu d)	1.71	3.56	3.44	3.86
D.N. e)	(~0)	2.7	14.1	27

a) Observed value at 50 °C.
b) extrapolated value to 25 °C.
c) dielectric constant.
d) dipole moment.
e) Gutmann's donor number.[9]

Discussion

Mechanism of Racemization of Tris(acetylacetonato)germanium(IV). Absence of ligand isotopic exchange and of decomposition clearly indicates that the racemization proceeds *via* an intra-molecular mechanism. Independence of the rate constant on the complex and the ligand concentration also supports such a mechanism.

An intra-molecular mechanism can proceed with or without break of one of the metal-ligand bonds. The former involves an intermediate with a unidentate ligand and the latter that with tris-bidentate ligands. It is difficult, however, to give a direct evidence for distinguishing them, and the discussion should be based on indirect evidences as follows.

The racemization was catalysed by acetic acid in TCE and by pyridine in AN. It is not likely that an acid or a base gives catalytic effect on the twisting of the complex without bond-break. Further, the racemization rate was found to increase with increase in ionic strength. It is likely that increase in ionic strength facilitates the bond break resulting in charge separation.

The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are not very different from one another in various solvents (Table 2), and the overall mechanism should not be very different in all of them, although the above observations were mainly made in AN. As Table 2 shows, the dielectric constant and the dipole moment do not seem to play an important role in determining the racemization rate. It seems that the rate increases and $\Delta H^{\ddagger}$ decreases with increase in donor number[9] of the solvents. The donor number reflects the ease with which the solvent molecules have interaction with the central metal ion, and its increase would facilitate the break of Ge–O bond of the complex. In those solvents with bigger donor numbers, even decomposition of the complex was observed to produce free acetylacetone.

On the basis of these facts, we propose a racemization mechanism involving an intermediate with a unidentate ligand, as shown in Fig. 6. Such a mechanism can have either the bond break or the succeeding intra-molecular rearrangement as rate-determining step. Although a direct evidence is given with difficulty, we tend to think that the rate-determining step would be the solvent-assisted break of the first metal-ligand bond. If the solvent molecules did not assist the bond break but just occupied the vacant coordination site of the intermediate, or if they gave an indirect effect to ease the break of ionic Ge–O bond, not the donor number but rather the dipole moment or the dielectric constant would be related to the rate and the activation enthalpy of the complex. Further, if the internal rearrangement were the rate determining step, the effect of the solvents would be reversed.

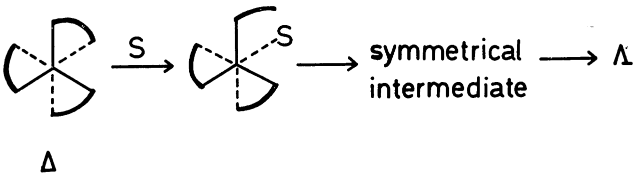

Fig. 6. Plausible reaction mechanism.
(The "symmetrical intermediate" can be either trigonal bipyramid or square pyramid, but its structure is not known from the present experiments.)

Holm and co-workers measured the coalescence of the proton signals of tris-type germanium(IV) complexes of substituted tropolonate in various chlorohydrocarbons by NMR, and discussed the mechanism of intra-molecular geometrical isomerization and racemization.[3] It was suggested that the intramolecular rearrangement proceeds without involving bond-break. They obtained $\Delta H^{\ddagger}$ values 12 to 17 kcal/mol and log A 12, which are common with those of other tris-α-diketonato complexes. Our $\Delta H^{\ddagger}$ values are significantly larger than theirs and our present racemization is more adequately presumed to have a different rate-determining step from theirs.

Comparison with Related Compounds. Tris(acetylacetonato)germanium(IV) gives very similar absorption and circular dichroism spectra to those of tris(acetylacetonato)silicon(IV). The $(-)_{589}$-isomer of $[Ge(acac)_3]^+$ can be assigned to absolute configuration Δ from comparison of the CD spectrum in the UV π-π^* transition region with that of tris(acetylacetonato)silicon(IV),[10] whose absolute configuration was supported by the CD spectrum[11] and X-ray crystallography of tris(catecholato)arsenic(V).[12]

The solubility of various salts of $[Ge(acac)_3]^+$ in various organic solvents is also very similar to that of $[Si(acac)_3]^+$ salts.

Table 1 shows the values of rate constants and activation parameters of racemization of $[Si(acac)_3]^+$, too. The ligand isotopic exchange of the silicon complex is also very slow. Its racemization is catalysed by acids in TCE and by bases in AN, and an intramolecular mechanism involving bond-break was proposed. The activation parameters for the germanium and silicon complexes are very near to each other. All these facts are reckoned as to reflect the overall similarity of these two elements.

A number of studies have been published concerning the kinetics of geometrical isomerization and racemization ("site-exchange") of α-[3,13] and β-diketonato[4] complexes of various metal ions. The site exchange is generally understood to proceed intra-molecularly in organic solvents, but various mechanisms have been proposed for their detailed progress. Examination of the references suggests that tris-β-diketonato complexes mostly undergo site exchange with one bond-break, whereas tris-α-diketonato complexes without bond-break. However, the experimental evidence for such a statement is rather indirect, and our present discussion provides more concrete support to the mechanism. Semi-empirical calculation on the basis of structural parameters also supports such a mechanism.[14] Most of these studies were made with chargeless complexes, but the discussion seems to be applicable to cationic complexes with +1 charge, *i.e.* our study with β- and Holm's with α-diketonatogermanium(IV).

The approximate order of overall site-exchange rate for tris-β-diketonato complexes of various metal ions is given below:[4]

$$\begin{aligned}&\mathrm{Fe(III),\ In(III)>Mn(III)>Ga(III)>Al(III)>Si(IV)}\gtrsim\\&\mathrm{Ge(IV)>Co(III)>Cr(III)>Ru(III)}\gtrsim\mathrm{Rh(III)}\end{aligned}\qquad(4)$$

The labilities of silicon(IV) and germanium(IV) complexes are larger than that of cobalt(III) complexes and smaller than those of Family IIIB elements. The activation enthalpies ($\Delta H^{\neq}$/kcal·mol^{-1}) involving bond-rupture process for site exchange of cobalt(III)[15] and aluminium(III)[16] are 20 to 30 and 15 to 20, and the log A's 14 to 16 and 13 to 17 respectively. The $\Delta S^{\neq}$ values are all positive. Although the present silicon and germanium complexes have +1 charge, the activation parameters for racemization are between those of Co(III) and Al(III) complexes. The sequence 4 seems to reflect the order of ease of break of the first metal-ligand bond.

On the other hand, ligand isotopic exchange studies suggested the break of the remaining bond of the unidentate ligand in the intermediate as rate-determining step. The rate of such inter-molecular reactions of octahedral β-diketonato complexes decrease approximately in the order,[5,8,17–19)]

$$\begin{aligned}&\mathrm{In(III)>Ga(III)>Al(III)>Co(III)>Si(IV),}\\&\mathrm{Ge(IV)>Cr(III)}\end{aligned}\qquad(5)$$

While the major part of this sequence is similar to sequence 4, silicon(IV) and germanium(IV) come next to cobalt(III). Such a difference may be related to the stability of the intermediate with five metal-ligand bonds. These ions with higher positive charge may interact with solvent molecules at the vacant coordination site more significantly to stabilize the intermediate.

The authors thank the Ministry of Education for Grant-in-Aid.

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