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Kinetics and Thermodynamics of the Racemization of Tris(L-valinato)chromium(III) Complexes in *N*,*N*-Dimethylformamide

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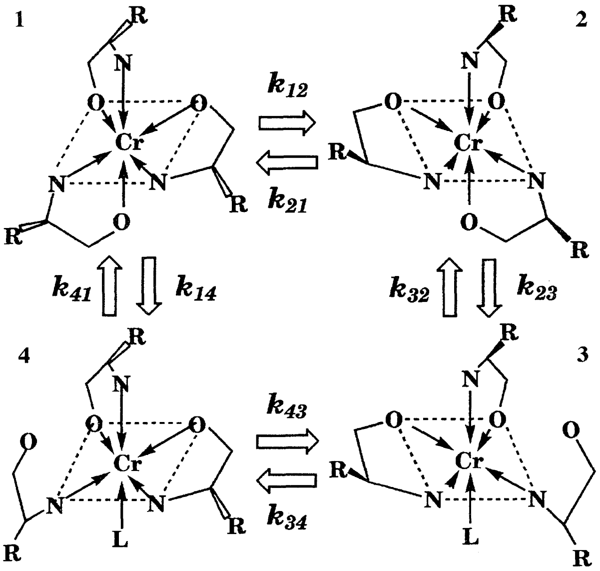
Racemization between *fac*-Λ-(+)$_{546}$- and *fac*-Δ-(−)$_{546}$-[Cr(val)$_3$] (**1** and **2**) was studied in *N*, *N*-dimethylformamide (DMF). These complexes were preferentially converted into bis-type complexes, Λ-(+)$_{546}$- and Δ-(−)$_{546}$-[Cr(val)$_2$(val-*N*)DMF] (**4** and **3**), and an equilibrium comprising these four species was established. In order to determine the equilibrium constants, rate constants, and activation parameters in a proposed square-network reaction system, the mole fractions of four species with time in reacting solutions at 40, 50, and 60 °C were determined by liquid chromatography. The reaction processes are discussed based on the obtained values.

We have already reported that the stereoselective preparation of *fac*-tris(L-α-amino acidato)chromium(III) complexes was observed in a solid- or liquid-phase reaction.[1—3] In view of the stereoselectivity, we have tried to prepare bis-type complexes, [Cr(amino acidato)$_2$(amino acidato-*N*)(solvent)], which involve both a monodentate L-α-amino acidato ligand with an amino-nitrogen as a donor atom and a polar solvent molecule as a ligand.[4] The bis-type complexes had a *cis-cis* structure with respect to the nitrogen or oxygen atoms, and were considered to be the precursor of *fac*-tris-type complexes produced in a liquid-phase reaction. Actually, the bis-type complexes gave precipitates of *fac*-tris-type upon standing in EtOH at room temperature.[4] While, during the course of studying the solution behavior of *fac*-tris-type complexes in DMF or Me$_2$SO, we have found that they resulted in equilibrated reacting solutions involving bis-type complexes (described previously), even at room temperature.[5]

We now report on interesting rearrangement reactions with the racemization of *fac*-[Cr(val)$_3$] in DMF as a typical example, and discuss the square-network reaction system (Scheme 1) based on thermodynamic and kinetic data.



Scheme 1. Square network reaction system with four kinds of (L-valinato)chromium(III) complexes. R and L designate the isopropyl group on valinato ligand and a DMF molecule as a ligand, respectively. k_{ij} is the first-order rate constant from complex *i* into *j*.

Experimental

Materials. *Fac*-Λ-(+)$_{546}$- or *fac*-Δ-(−)$_{546}$-[Cr(val)$_3$] (**1** or **2**) was prepared according to Ref. 1 or 3, respectively. Λ-(+)$_{546}$-[Cr(val)$_2$(val-*N*)DMF] (**4**) was prepared by dissolving Λ-(+)$_{546}$-[Cr(val)$_2$(val-*N*)Me$_2$SO] in DMF, which was prepared as previously reported,[4] and adding the resulting DMF solution into Et$_2$O. Crude Δ-(−)$_{546}$-[Cr(val)$_2$(val-*N*)DMF] (**3**) was obtained by dissolving the Λ-isomer (**4**) in MeOH and drying the resulting solution after 2 d. To obtain purer materials, concentrated DMF solutions of crude bis-type complexes were chromatographed on an acidic alumina column (Merck aluminium oxide 90 acidic, activity I, 3 cm i.d. ×20 cm) with DMF as an eluent. Elution gave three pink bands; the first two bands for Δ-(−)$_{546}$- and Λ-(+)$_{546}$-[Cr(val)$_2$(val-*N*)DMF] (**3** and **4**), however, were not well separated. The third (smaller) band comprised *fac*-[Cr(val)$_3$] (**1** and **2**), which was not eluted with pure DMF. Therefore, the fractions of the first two broader bands were followed by measuring the change in the optical rotation at 546 nm for every 2 ml; pure materials were obtained as precipitates upon adding the pure fractions for each isomer into Et$_2$O. Schematic drawings of these four species are shown in Scheme 1. At present, these structures have not yet been proved by X-ray crystallographic analysis, though the coordination of the solvent to the center chromium atom in the solid state of bis-type complexes (**3** and **4**) has been identified spectroscopically.[4]

Liquid Chromatography (LC). In order to determine the mole fractions of four kinds of complexes (**1**, **2**, **3**, and **4**) in the starting materials and reaction mixtures, LC with an aminopropyl-silica column (CHEMCOSORB 7NH$_2$, 4.6 mm i.d. ×150 mm, Chemco, Japan) and DMF eluent was used as reported previously.[6]

Kinetic Measurements. The reaction rates were measured by determining the mole fractions of each complex in quenched reaction mixtures. Four kinds of complexes (ca. 0.05 mmol, respectively) as starting materials were dissolved in 50 ml of DMF, and fifteen 3 ml aliquots of each solution were transferred into 5 ml glass ampules and shielded. An isothermal reaction was started by immersing these ampules into thermostated water baths maintained at 40, 50, and 60 °C. Each ampule was taken out of the bath at certain time intervals and immediately cooled in ice-water, after which an LC measurement for each sample was carried out. Atomic absorption spectrometry was also used to determine the total concentration of chromium(III) complexes in DMF, if necessary.

Results and Discussion

Thermodynamic Behavior. At first, the reaction behavior of complexes **1** and **2** in DMF were followed by the UV-vis absorption spectra and optical rotation measurements with time. Figure 1 shows the absorption spectral changes for complex **1** in DMF at 50 °C, which appeared to change with some isosbestic points. Irrespective of the kind of starting material, all of the reacting solutions finally gave similar spectra in shape to those of complexes **3** and **4**, and showed negative rotations at 546 nm. These results implied that the reacting solutions had attained equilibria with several species involving complex **3** as a main product. Therefore, the separation and identification of the reaction products were attempted by LC after the elapse of ample time.[6] All of the reacting solutions showed analogous chromatograms; a typical chromatogram is shown in Fig. 2, where complex **1** was chosen as a starting material. Each complex was eluted in the order **3**, **4**, **2**, and **1**; it was ascertained that four complexes at equilibria were present by the mole fractions, $\mathbf{3}:\mathbf{4}:\mathbf{2}:\mathbf{1} \fallingdotseq 0.62:0.31:0.06:0.01$. Also, the amounts of other products were less than that of complex **1**, if present. Thus, the square-network reaction systems as shown in Scheme 1, was expected for the stereochemical rearrangement reactions among these four species.

The equilibrium constants (K_{ij}) calculated from the mole fractions of species i and j at equilibria in reaction mixtures maintained at 60 and 50 °C for 1 d, and 40 °C for 3 d, were $K_{12}=5.2$ ($s=1.0$), $K_{23}=10.8$ ($s=1.1$), $K_{34}=0.51$ ($s=0.03$), and $K_{41}=0.037$ ($s=0.013$), where s is the sample standard deviation. Since the obtained K_{ij} values did not appear to depend on the starting materials or temperature, the standard reaction Gibbs energies of the four equilibrium processes seemed to be essentially entropic. As for the superiority of bis-type complexes against tris-type ones regarding stability, it could be readily predicted that the mobility of a monodentate valinato ligand in complex **3** or **4** was associated with an increase in entropy. However, in order to explain why the entropical stability of Δ-type complex **2** or **3** was superior to that of Λ-type complex **1** or **4**, we needed to consider the steric effect on the difference in the geometrical configuration between two types, that is, the difference in the solvation structures. Regarding the configuration of complex **2**, three amino-groups are surrounded by bulky side-chains (isopropyl group) of valinato ligands and shielded from solvents. In contrast, the interaction between a polar solvent and amino-hydrogen could be sufficiently expected for complex **1**. A similar tendency was expected for the case of complex **3** or **4**, whose interaction might be weaker. That is, the difference among the stabilities of four complexes in DMF probably reflects the differences in the degree of freedom of the ligands, and in the solvation entropies of the DMF molecules for their complexes. Though both tris- and bis-type complexes have the same facial configuration [Cr(O)$_3$(N)$_3$] with respect to the donor atoms of ligands, there should be some differences in the enthalpy values, due to the different ligand fields between the two types of complexes. Accordingly, the standard reaction enthalpy values of zero must consequently occur due to the fact that various factors, such as the solvation enthalpy, cancel out each other.

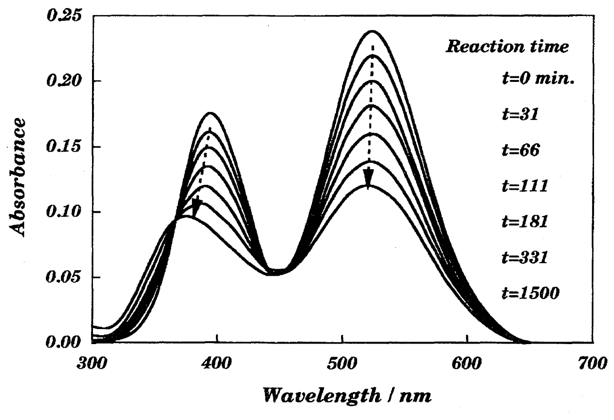


Fig. 1. UV-vis spectral change with time of 1 mmol dm^{-3} complex **1** in DMF at 50 °C. Trends of the spectral change are shown by arrows.

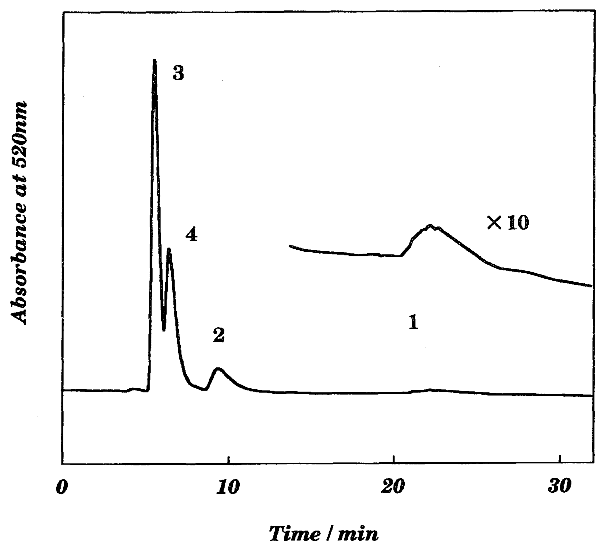


Fig. 2. Chromatogram of the DMF solution of complex **1** equilibrated at 50 °C. Column; CHEMCOSORB 7NH$_2$ (4.6 mm i.d. ×150 mm, Chemco, Japan), mobile phase; DMF, flow rate; 0.5 ml min^{-1}.

With respect to the difference in stability between the Λ- and Δ-type complexes, Gillard and Payne had reported on the superiority of the Δ-type complex against the Λ-type one regarding the thermodynamic stability ($\Lambda/\Delta=40/60$) in the racemization of *mer*-[Co(val)$_3$] in boiling EtOH with activated charcoal.[7] They also pointed out the steric hindrance by a more bulky substituent on the α-carbon atom in the transition state, concerning the extremely small yields of facial isomers compared to those of meridional ones in the preparation of [Co(val)$_3$],[7] although meridional isomers have never been obtained in the preparation of chromium(III) complexes. We cannot at present discuss the difference or similarity of the solution behavior between chromium(III) and cobalt(III) complexes in detail.

Kinetic Behavior. An isothermal reaction with each complex as a starting material was carried out, and the variations in the mole fractions of four complexes with time were followed by LC measurements in order to determine the rate constants (k_{ij}). As an example, the mole fraction-time curves for four complexes at 50 °C are shown in Fig. 3, where complex **1** was chosen as the starting material. These curves were analyzed by the combined use of numerical integration and a least-squares method based on the square-network shown in Scheme 1; eight rate constants (Table 1) were obtained.[5] Further, the standard enthalpies of activation ($\Delta H^{\neq}$) and the standard entropies of activation ($\Delta S^{\neq}$) were also deduced from Eyling-plots, whose values are collected in Table 2.

In a stereochemical rearrangement of the geometrical and optical isomers of octahedral complexes containing three didentate ligands, two basic pathways are generally considered: twist and bond-rupture mechanisms. In the case of *fac*-[Cr(val)$_3$] in DMF, it was thought that the process $\mathbf{1}\rightleftarrows\mathbf{2}$ could be attributed to the former, and the process $\mathbf{1}\rightleftarrows\mathbf{4}\rightleftarrows\mathbf{3}\rightleftarrows\mathbf{2}$ corresponded to the latter. Considering that only facial isomers could be obtained in the [Cr(val)$_3$] system, the possible pathway in the process $\mathbf{1}\rightleftarrows\mathbf{2}$ was confined to be a twist mechanism about the real-C_3 axis through an intermediate, as shown in Fig. 4(a). While, the bond-rupture mechanism involves five-coordinated intermediates with a square-pyramidal (SP) or trigonal-bipyramidal (TBP) structure,[8,9] and every kind of isomer ought to be produced rapidly through a rearrangement to the TBP-basal, TBP-apical or SP-apical state from the SP-basal transition state (Fig. 4(b)) generated by a breaking of the Cr–O bond. However, the preponderance of complexes **3** and **4** in DMF indicated that a polar DMF molecule rapidly occupied the vacated site in the SP-

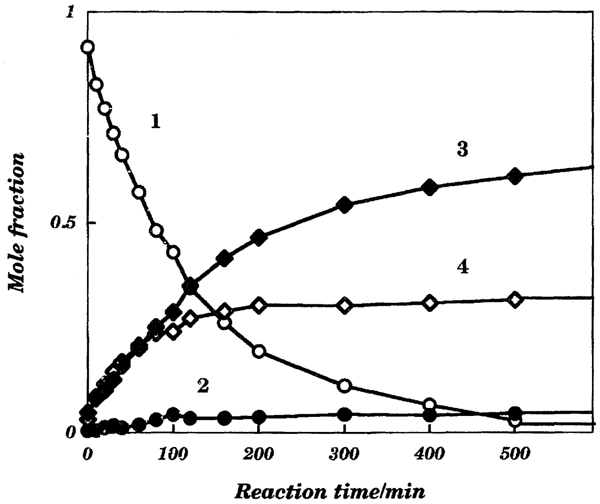


Fig. 3. Time course of the thermal reaction of complex **1** in DMF at 50 °C.

Table 2. Standard Enthalpies ($\Delta H^{\neq}$) and Entropies ($\Delta S^{\neq}$) of Activation in DMF, 313—333K

Process	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}
$\mathbf{1}\rightarrow\mathbf{2}$	86.4	−75.7
$\mathbf{2}\rightarrow\mathbf{1}$	86.4	−88.1
$\mathbf{2}\rightarrow\mathbf{3}$	98.2	−16.6
$\mathbf{3}\rightarrow\mathbf{2}$	98.1	−37.4
$\mathbf{3}\rightarrow\mathbf{4}$	86.3	−54.0
$\mathbf{4}\rightarrow\mathbf{3}$	86.3	−48.2
$\mathbf{4}\rightarrow\mathbf{1}$	94.4	−55.7
$\mathbf{1}\rightarrow\mathbf{4}$	94.5	−29.1

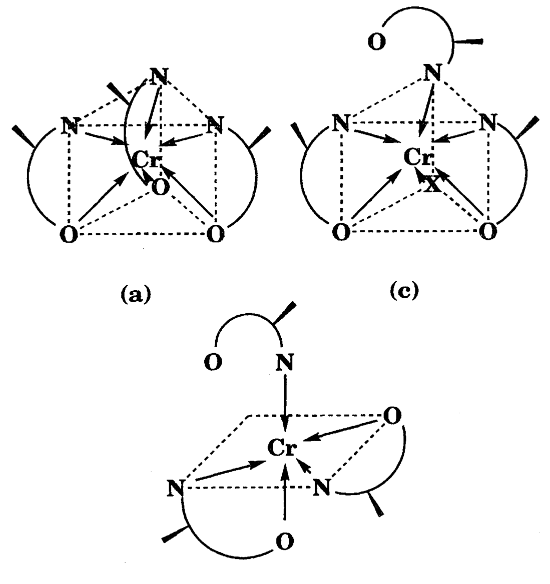


Fig. 4. Transition states in racemization of *fac*-[Cr(val)$_3$]. (a); trigonal-prismatic state in twist mechanism around the real-C_3 axis, (b); SP-basal state in bond-rupture mechanism, (c); trigonal-prismatic state in twist mechanism around the pseud-real-C_3 axis, where X designates a donor oxygen atom of DMF.

Table 1. Rate Constants in DMF

T/K	$k_{12}/10^{-6}$s^{-1}	$k_{21}/10^{-7}$s^{-1}	$k_{23}/10^{-5}$s^{-1}	$k_{32}/10^{-6}$s^{-1}	$k_{34}/10^{-5}$s^{-1}	$k_{43}/10^{-5}$s^{-1}	$k_{41}/10^{-6}$s^{-1}	$k_{14}/10^{-5}$s^{-1}
313	2.90	6.33	3.51	3.12	4.08	8.16	1.37	3.51
323	8.37	18.28	11.71	10.39	10.59	21.17	4.78	12.25
333	22.63	49.41	35.96	31.90	31.82	63.63	12.83	32.90

basal state, and that bis-type complexes as an intermediate were consequently stabilized. Namely, the rearrangement to the next state from SP-basal after a bond-rupture could not occur, and only the racemization process $\mathbf{3}\rightleftarrows\mathbf{4}$ proceeded with a twist motion about the pseud-real-C_3 axis through an intermediate, as shown in Fig. 4(c). Consequently, also in the process $\mathbf{1}\rightleftarrows\mathbf{4}\rightleftarrows\mathbf{3}\rightleftarrows\mathbf{2}$, the meridional isomers cannot be produced. Further, it was imagined that the twist motion about an imaginary-C_3 axis in the twist process ($\mathbf{1}\rightleftarrows\mathbf{2}$ or $\mathbf{3}\rightleftarrows\mathbf{4}$) was inhibited by a steric hindrance due to bulky side-chains. A further investigation into the reaction processes mentioned above, which might result from the characteristic of chromium(III) atom, has now been extended to the *fac*-[Co(val)$_3$] system.

Although many kinetic studies have been reported concerning the optical and geometrical isomerizations of octahedral metal(III) complexes, no solvolysis reactions similar to those ($\mathbf{1}\rightarrow\mathbf{4}$ and $\mathbf{2}\rightarrow\mathbf{3}$) observed in this system have been reported. Also, the racemization rate has been little reported, compared with isomerization between the meridional and facial isomers. The remarkable feature shown in Tables 1 and 2 is now briefly discussed. Although the $\Delta H^{\neq}$ values for two twist processes, $\mathbf{1}\rightleftarrows\mathbf{2}$ and $\mathbf{3}\rightleftarrows\mathbf{4}$, were approximately equal, this equivalence seemed strange, considering the difference in the number of chelate-rings between the bis-type and tris-type complexes. For example, the possibility of hydrogen-bonding between a carboxyl group of the monodentate valinato ligand and an amino group of the adjacent didentate one must be considered in order to explain these data. In any case, further information concerning the configurations of complexes **3** and **4** in connection with the difference in the $\Delta S^{\neq}$ values must be given in order to explain these data explicitly. The reattachment of the dangling monodentate ligand to the center chromium atom ($\mathbf{4}\rightarrow\mathbf{1}$ and $\mathbf{3}\rightarrow\mathbf{2}$) proceeded very slowly compared with the solvolysis from the tris-type to bis-type species ($\mathbf{1}\rightarrow\mathbf{4}$ and $\mathbf{2}\rightarrow\mathbf{3}$). The large difference in the rates between these mutually reverse processes, such as $\mathbf{4}\rightarrow\mathbf{1}$ and $\mathbf{1}\rightarrow\mathbf{4}$, must also be attributable to the difference in the $\Delta S^{\neq}$ values. Since these results indicated the importance of the solvation energy of polar DMF molecules, we must quantitatively discuss the electrostatic interaction between the polar-complex molecules and the polar-solvent ones from now on.

As described above, in this new equilibrium system the interaction between polar solvents and L-α-amino acidato ligands is very important. It is thus of interest to see how the structure of the side-chains on their ligands or the polarity of the solvent affects the stability of each complex or the rate of respective reaction process. In order to elucidate these respects, further studies with other L-α-amino acids or other polar solvents are now proceeding in our laboratory. A more detailed report concerning these results will be given elsewhere.

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