



Article

Chiral Tectonics: VCD and ECD Application for Epimerization of a Star-Burst Tetranuclear Complex with a Labile Central Core

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Abstract: The present article reports the application of vibrational circular dichroism (VCD) and temperature-dependent electronic circular dichroism (ECD) methods to reveal the dynamical aspects of a star-burst tetranuclear metal complex with a labile central core in a solution. One-handed chiral inert tecton, Δ - or Λ -[Ru(III)(acac)₂(taetH)] (acacH = acetylacetonate, taetH₂ = tetraacetylthane), was prepared by reacting [Ru(acac)₃] with taetH₂ in solid at 120 °C. The $\Delta\Lambda$ -pair of pure enantiomers was obtained chromatographically. On adding Al(ClO₄)₃ to its enantiopure solution, three units of one-handed tecton were assembled spontaneously around an aluminum(III) ion to form a star-burst tetranuclear complex, [(Δ - or Λ -Ru(acac)₂(taet))₃Al(III)]. The VCD spectrum recorded on the CDCl₃ solution of the complex showed that the central chirality around an Al(III) ion took dominantly the absolute configuration antipodal to those of peripheral Ru(III) units at the temperature lower than −10 °C. The complex underwent interconversion between the Δ - and Λ -configurations around a central Al(III) core (or epimerization) in solution. The activation energy barrier was determined from the time courses of ECD spectra in CHCl₃ and CH₃OH.

Keywords: vibrational circular dichroism; temperature-dependent electronic circular dichroism; epimerization; tetranuclear complex; β -diketonato; Ru(III); Al(III); chiral; $\Delta\Lambda$ isomers; chiral tectons

1. Introduction

Tris(chelated) metal complexes with β -diketonato ligands have demonstrated a wide application in the fields of asymmetric catalysis, electrochemical mediators, metal oxide frameworks (MOF), and so on [1–8]. In addition to the unique properties as a mononuclear complex, novel stereochemical aspects immerse when a labile metal ion is incorporated into these units. The situations are even more interesting when chiral elements are involved in multi-nuclear systems. The dynamical control of such chiral properties is an attractive issue in constructing the supramolecular architectures of metal complexes.

One approach taken in this area is so-called molecular tectonics [8]. According to the method, one-, two-, or three-handed units (or tectons) are connected to construct molecular frameworks systematically [9]. When chirality is introduced into each tecton, the organized systems might exhibit various levels of chirality from molecular to macromolecular scales. We have employed the $\Delta\Lambda$ isomerism of a tris(chelated) complex as a chiral motif with D_3 symmetry in the tectonics approach [5]. A mononuclear complex with empty coordinating sites is possible to play a role of a tecton. On this basis, tris(acetylacetonato)ruthenium(III) ([Ru(III)(acac)₃]) was reacted with tetra acetylthane (taetH₂) in solid states. It lead to the production of mixed ligand complexes such as [Ru(acac)_n(taetH)_{3−n}]

(acac = acetylacetonato; taetH = singly protonated tetraacetylethanato; $n = 2, 1$ and 3 , respectively). They were expected to play roles of one-, two-, and three-handed chiral tectons, respectively (Chart 1). Various types of multi-nuclear complexes were prepared by connecting these tectons with an inert or labile metal ion such as Al(III), Fe(III), Ni(II), Ru(III), and Pd(II) [10–14]. As a result of using chiral tectons, the resultant systems exhibited supramolecular chirality.

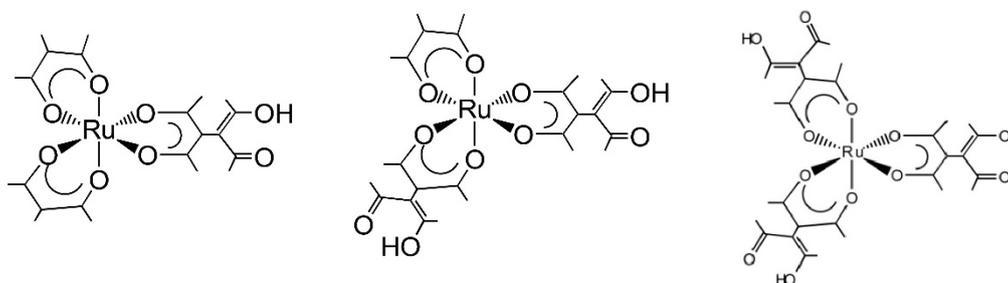


Chart 1. The molecular structures of **(left)** Inert chiral one-handed tecton (Δ -Ru(III)(acac)₂(taetH))(acac = acetylacetonato; taetH = singly protonated tetraacetylethanato), **(middle)** two-handed tecton (Λ -Ru(III)(acac)(taetH)₂), and **(right)** three-handed tecton (Λ -Ru(III)(taetH)₃).

In case of inert one-handed tecton (Chart 1 (left)), a star-burst tetranuclear complex was formed spontaneously by adding a labile metal ion such as Al(III) to a methanol solution of Δ - or Λ -[Ru(III)(acac)₂(taetH)]. The previous communication demonstrated that the locking of an octahedral core around a central metal ion is achieved in a solid state, in which tetranuclear complexes are stacked with their three branches interdigitated [10]. When the complex was dissolved in methanol, it underwent epimerization or the central core interconverted from Δ to Λ or vice versa. The process was monitored by means of ¹H-NMR and electronic circular dichroism (ECD) measurements [10,11].

In these years, we have been pursuing the possible utility of the vibrational circular dichroism (VCD) spectroscopy to reveal the stereochemical aspects of transition metal complexes [15–18]. VCD measures the differential absorption of left versus right circularly polarized IR radiation for molecular vibration transitions for metal complexes [19–25]. The detailed conformation of a molecule is determined by comparing the experimental and theoretical results concerning a large number of VCD peaks.

In this paper, we have studied the dynamical aspect of [Δ -Ru(III)(acac)₂(taetH)]₃Al(III) or [Λ -Ru(III)(acac)₂(taetH)]₃Al(III) (Chart 2) by VCD and temperature-dependent ECD. The possible configurations are considered as Chart 3. The central core and anyone of three peripheral moieties was Δ - Λ (or Λ - Δ hetero-chiral connection) or Δ - Δ (or Λ - Λ homo-chiral connection). The absolute configuration of a central labile core was confirmed by VCD. The potential barrier for epimerization was estimated by obtaining the rate of epimerization in the wide range of temperature. As far as our literature survey is concerned, this was the first attempt to follow the structural change of the limited domain in a chiral multi-nuclear metal complex by means of VCD spectroscopy.

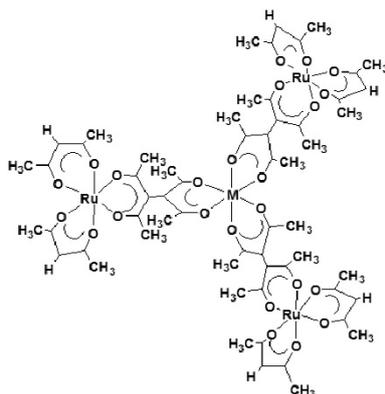


Chart 2. A star-burst tetranuclear complex of $[\{\text{Ru(III)(acac)}_2(\text{taet})\}_3\text{M(III)}]$.

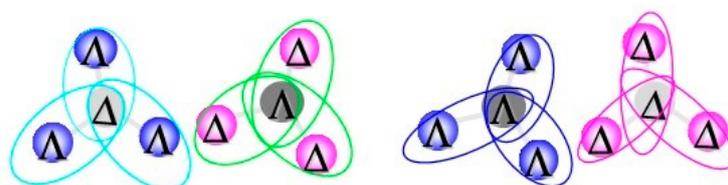


Chart 3. Illustrating a star-burst tetranuclear complexes with inert three peripheral and labile central core. Hetero-chiral (**left**) and home-chiral connections (**right**).

2. Results

2.1. Preparation of a Star-Burst Tetranuclear Complex

A star-burst tetranuclear complex was prepared as described previously [10]. Three equivalents of enantiopure one-handed tecton, Δ - or Λ - $[\text{Ru(III)(acac)}_2(\text{taetH})]$, was dissolved in methanol. One equivalent of $\text{Al}(\text{NO}_3)_3$ and ten equivalents of trimethylamine were added to the solution. The solution in an open vial was stirred at room temperature for a week until the whole solvent was evaporated. The NMR spectrum of the CDCl_3 solution of the precipitate confirmed the formation of a tetranuclear complex, $[\{\text{Ru(III)(acac)}_2\text{taet}\}_3\text{Al(III)}]$.

2.2. Time-Dependent ECD Spectra

Figure 1 shows the change of the ECD spectrum of $[\{\Lambda\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ with time after a small amount of the solid precipitate as prepared above was dissolved in CH_3OH at room temperature and 0°C . The ECD peaks at 280 nm, 360 nm and 430 nm were due to the moieties of $\{\Lambda\text{-Ru(III)(acac)}_2(\text{taet})\}$. They kept their intensity at a constant level with time. The ECD peak at ca. 320 nm arose from the unbalancing of Δ - and Λ -configurations of the central labile core. When the sign of the peak was compared with the reported ECD spectrum of enantiomeric $[\text{Al(III)(acac)}_3]$ at -78°C [26], an Al(III) ion in $[\{\Delta\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ was suspected to take the Λ -configuration dominantly. The validity of this assignment was examined by use of VCD as described in the later section.

The ECD peak at ca. 320 nm decreased with time until it disappeared after the elapse of sufficient time (ca. 1 h). The results implied that the central labile core of Al(III) in $[\{\Lambda\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ epimerized slowly to a diastereomeric mixture of Λ - and Δ - $[\{\Lambda\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$. These diastereomers were concluded to be present in an equal amount in the equilibrium state.

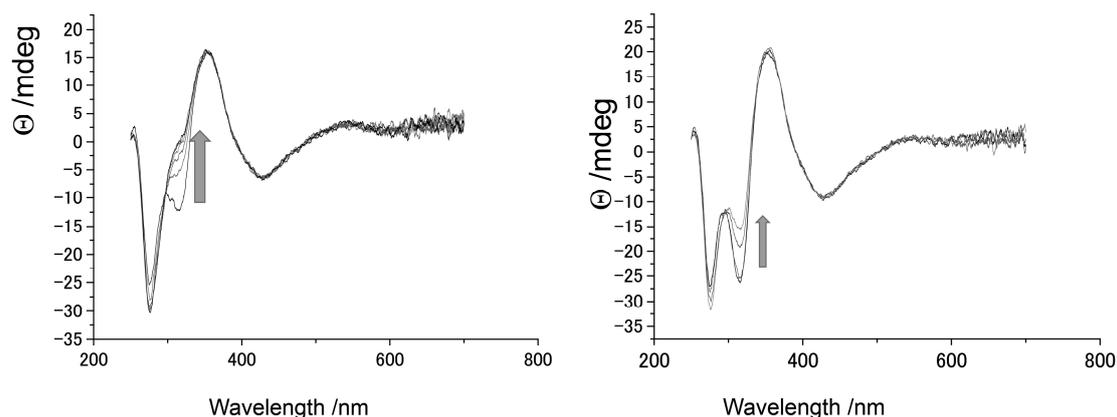


Figure 1. The time change of the ECD spectrum of a methanol solution containing $[\{\Lambda\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ at room temperature (**left**) and $0\text{ }^\circ\text{C}$ (**right**). The spectra were recorded at 3, 5, 8, 10, 13, and 15 min (upper) and 3, 8, 30 and 50 min (lower) after dissolving the solid.

2.3. Epimerization Rate Constants Using Temperature-Dependent ECD

Comparing the ECD spectra between $0\text{ }^\circ\text{C}$ and room temperature, the rate of epimerization depended on the temperature remarkably. The time-change of the ECD spectrum was monitored in the temperature range from $-10\text{ }^\circ\text{C}$ to $35\text{ }^\circ\text{C}$. The monitoring wavelength was 318.8 nm as selected from the results of Figure 1. The effects of medium were studied using CH_3OH and CH_3Cl as a solvent. The examples were shown in Figure 2 in case of $[\{\Lambda\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ in CHCl_3 . The rate constant was calculated by fitting the experimental curves according to the following Equation (1):

$$R = Ae^{-2kt}, \quad (1)$$

in which R is the change of ECD peak intensity, A the initial amplitude, and k the unimolecular rate constant of epimerization. The kinetic results are summarized in Table 1.

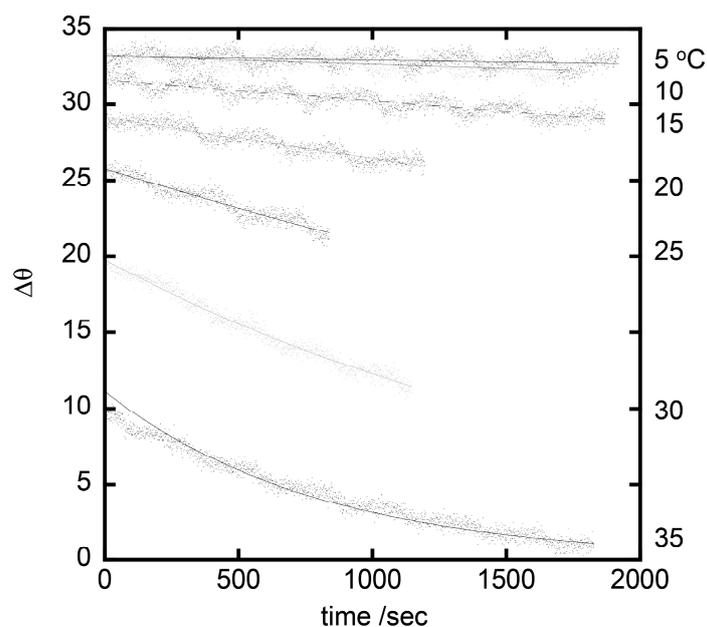
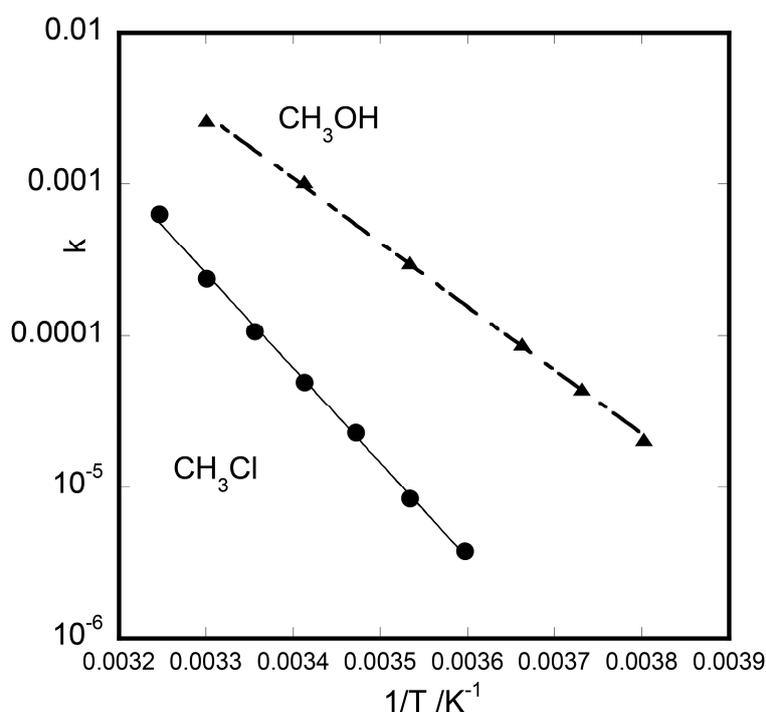


Figure 2. The time change of the electronic circular dichroism (ECD) spectrum of a chloroform solution of $[\{\Lambda\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ at monitoring wavelength of 318.8 nm . The temperature was $5, 10, 15, 20, 25, 30,$ and $35\text{ }^\circ\text{C}$ from the top to the bottom.

Table 1. The unimolecular rate constant of epimerization of $[\{\Delta\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ in CHCl_3 and CH_3OH .

Temperature	CHCl_3 (sec^{-1})	CH_3OH (sec^{-1})
-10	-	2.05×10^{-5}
-5	-	3.31×10^{-5}
0	-	8.78×10^{-5}
5	3.77×10^{-6}	-
10	8.36×10^{-6}	3.04×10^{-4}
15	2.28×10^{-5}	-
20	4.91×10^{-5}	1.03×10^{-3}
25	1.06×10^{-4}	-
30	2.39×10^{-4}	2.65×10^{-3}
35	6.32×10^{-4}	-

Figure 3 shows the Arrhenius plots of the unimolecular rate constants in CH_3Cl and CH_3OH . From the slope of each plot, the activation energy of epimerization was obtained to be ca. 120 kJ/mol and 81 kJ/mol in CHCl_3 and CH_3OH , respectively. The results indicated that energy barrier for epimerization was higher for a less solvating solvent (CH_3Cl) than for more solvating one (CH_3OH).

**Figure 3.** The Arrhenius plots of epimerization rate constants of $[\{\Delta\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ in CH_3OH or CH_3Cl as indicated.

2.4. VCD Application for the Epimerization

The absolute configuration of the labile core of Al(III) in $[\{\Delta\text{- or } \Lambda\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ was attempted to be determined by means of the VCD method. Figure 4a,b show the VCD and IR spectra of $[\{\Delta\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ and $[\{\Lambda\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ in CDCl_3 . Nearly the mirror image relation was observed between the two diastereomeric pairs. The VCD peaks were so high that the clear spectra were obtained in the short period of scanning (ca. 1000 scans). This made it possible to measure the VCD spectra of a labile molecule like the present tetranuclear complexes. As was previously established theoretically, the VCD absorption of a tris(β -diketonato)ruthenium(III)

complex was highly enhanced through the participation of the low-lying excited states of Ru(III). Its paramagnetic nature was a main factor for inducing such enhancement [13,15,16]. The only baseline correction made in the present measurements was to subtract the VCD spectra of CDCl_3 alone from the observed spectra. No further correction such as the averaging the spectra of antipodal samples (or $(R + S)/2$) was performed to obtain the base line. For comparison, the VCD and IR spectra were calculated for $[\{\Delta\text{-Ru(III)(acac)}_2(\text{taet})\}_3\Lambda\text{-Al(III)}]$, as shown in Figure 4c. The experimental spectra were in satisfactory agreement with the calculated ones as corresponded by the number of each peak (Figure 4a). According to the CD and VCD, the star-burst tetranuclear complex were concluded to include only the hetero-chiral (or $\Delta\text{-}\Delta$ or $\Lambda\text{-}\Lambda$) connections between the peripheral and central parts.

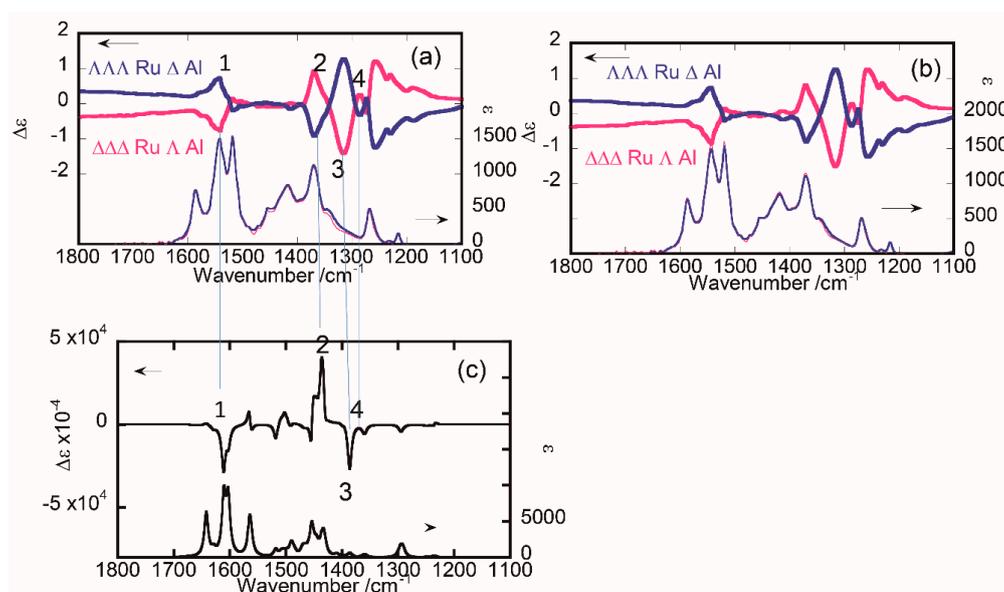


Figure 4. Vibrational circular dichroism (VCD) and IR spectra: (a) initial 10 min (b) final 1.5 h. $[\{\Delta\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ (blue) or $[\{\Delta\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ (red) in CDCl_3 (c) the calculated VCD and IR spectra of $[\Delta\text{-Ru(III)(acac)}_2(\text{taet})\}_3\Lambda\text{-Al(III)}]$ in a gas phase.

The VCD spectra varied with time. The difference between the initial (ca. 10 min) and final (ca. 1.5 h) spectra was calculated as shown in Figure 5a. The signal-to-noise ratio for main peaks in the difference spectra was of the order of 10 so that the peaks were regarded as true ones with sufficient reliability. Each peak was numbered in order to make correspondence between the experimental and theoretical spectra. For comparison, the VCD and IR spectra of $\Delta\text{-}$ and $\Lambda\text{-}[\text{Al(III)(acac)}_3]$ were calculated as shown in Figure 5b. The couplet peaks around $1300\text{--}1400\text{ cm}^{-1}$ peaks are assigned to the stretching vibrations of C–C–C and C=O in the bridging parts between the peripheral and central core regions. When a tris(chelated) complex maintains the D_3 symmetry, no splitting occurs for the peaks as assigned to degenerated E-state. Experimentally, however, the peaks were split into two (a and b). It implied that the D_3 symmetry was broken in the present tetranuclear complex. The signs of the couplet peaks were well coincident between the experimental and calculated spectra. This leads to the conclusion that the absolute configuration of the central core in $[\Delta\text{- or } \Lambda\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ was Λ or Δ , respectively. It was in accord with the conclusion from the ECD spectra. In other words, the peripheral Ru(III) moieties tended to lock the configuration of the central labile core in the antipodal manners.

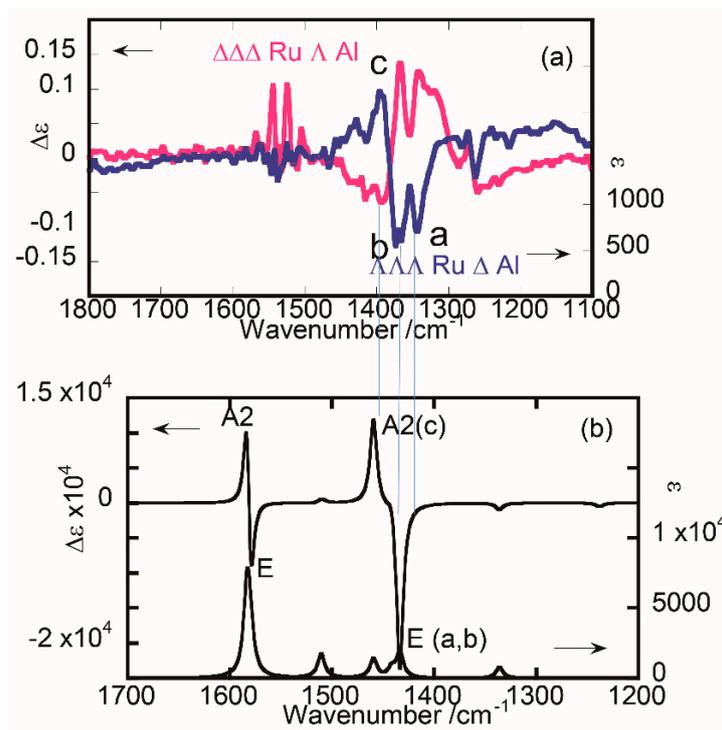


Figure 5. (a) Difference of VCD spectra between the initial and final states: (blue) $[\{\Delta\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ or (red) $[\{\Delta\text{-Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ in CDCl_3 . (b) The calculated VCD and IR spectra of $\Delta\text{-[Al(III)(acac)}_3]$ in a gas phase.

3. Discussion

The present work revealed the dynamics of $\Delta\text{-}$ (or $\Lambda\text{-}$) $[\{\Delta\text{-}$ (or $\Lambda\text{-}$) $\text{Ru(III)(acac)}_2(\text{taet})\}_3\text{Al(III)}]$ in solutions. The activation energy of the following epimerization reaction was obtained to be $119.6 \text{ kJ}\cdot\text{mol}^{-1}$ and $81.1 \text{ kJ}\cdot\text{mol}^{-1}$ in CHCl_3 and CH_3OH , respectively:



Since the ECD absorption due to the chirality of the central core diminished completely in the equilibrium state, it was concluded that there was little energy difference between the above diastereomeric forms. The potential barrier for epimerization was thought to arise from the step of the partial dissociation of Al–O bonds to cause the rearrangement of the Ru(III) moieties. The fact that a more solvating solvent (CH_3OH) gave smaller activation energy than a less solvating solvent (CHCl_3) suggested that such dissociation was assisted by the intervening of solvent molecules.

As another noteworthy aspect, the VCD method was proved to be an effective tool to determine the absolute configuration of even a labile molecule in a solution. This was accomplished that the observed VCD peaks were high and that the measurements were performed within a short period of time. In addition to the above aspect, the VCD spectra were possible to provide detailed information of the conformation of a multi-nuclear complex in a solution.

We have previously reported the VCD spectra of eight inert diastereomers of $\Delta\text{-}$ (or $\Lambda\text{-}$) $[\{\Delta\text{-}$ (or $\Lambda\text{-}$) $\text{Ru(III)(acac)}_2(\text{taet})\}_3\text{Ru(III)}]$ [13]. In analyzing the spectra, an attention was paid to the band around 1550 cm^{-1} , which was assigned to the stretching modes of two C–O bonds in a β -diketonato ring. It was deduced that the sign of the VCD peak reflected the chiral character of the vibrational motion localized on the C–O bonds. Particularly the spectral features of the peaks depended on whether the part connecting the central core and anyone of three peripheral moieties was $\Delta\text{-}\Delta$ (or $\Lambda\text{-}\Lambda$ homo-chiral connection) or $\Delta\text{-}\Lambda$ (or $\Lambda\text{-}\Delta$ hetero-chiral connection). Peripheral parts were

called the homo- and hetero-chiral connections (Chart 3), respectively. In the present star-burst complexes of $[\{\Delta\text{-Ru}(\text{acac})_2(\text{taet})\}_3 \Delta\text{-Al}]$ and $[\{\Lambda\text{-Ru}(\text{acac})_2(\text{taet})\}_3 \Delta\text{-Al}]$, the number of homo- and hetero chiral connections are 0 and 3, respectively. The signs of the VCD spectra observed around 1300 cm^{-1} (No. 4 in Figure 4a) were in accord with the hetero-chiral connections of Δ - (or Λ -) $[\{\Delta$ - (or Λ -) $\text{Ru}(\text{III})(\text{acac})_2(\text{taet})\}_3 \text{Ru}(\text{III})]$ [13]. In other words, the central labile core around an Al(III) atom was revealed to be locked in the antipodal chirality (Chart 3 (left)). Such a locking was achieved due to the molecular stacking in a solid state.

As a new finding of the present work, the time-variable parts in the ECD and VCD spectra were revealed to reflect the interconversion of the central part in a multi-nuclear metal complex. The attempts obtaining the solid-state VCD and temperature-dependent VCD evidences for the chiral locking of the present compounds are now under progress.

4. Materials and Methods

A chiral one-handed tecton, Δ - (or Λ -) $[\text{Ru}(\text{III})(\text{acac})_2(\text{taetH})]$, was synthesized and optically resolved chromatographically on a chiral column as reported previously [10]. The star-burst tetranuclear complex was synthesized by reacting the tecton with Al(III) simultaneously according to the reported method [10]. Electronic absorption and circular dichroism spectra were measured with a U-2810 spectrophotometer (Hitachi, Tokyo, Japan) and a J-720 spectropolarimeter (JASCO, Tokyo, Japan). ECD spectra were measured with a J-720 (JASCO, Tokyo, Japan) equipped with a temperature-controlling cell holder Unispeks (UNISOKU, Oosaka, Japan). VCD spectra were measured by VCD/RAS spectrometer (JASCO PRESTO-S-2007) at room temperature. A liquid cell with BaF_2 windows and 0.15 m spacer was used. Resolution of both IR and VCD spectra was 4 cm^{-1} . The VCD signals were accumulated about 5000–10,000 times. The scanning time was short in comparison to the VCD measurements of organic compounds. This was because the Ru(III) moieties in the present tetranuclear complexes exhibited enhanced VCD signals due to their low-lying excited states [13]. No artificial correction of the original data such as smoothing or middle-point averaging the antipodal samples was made in the VCD spectra. The baseline correction was made by subtracting the spectrum of a solvent (CDCl_3) from the spectrum of each sample. The reliable signal was obtained with high signal-to-noise ratio, or S/N was in the range of 100~1000 for the original spectra. The difference spectra showed S/N = 5~8.

The IR and VCD spectra of Δ - $[\text{Al}(\text{III})(\text{acac})_3]$ and $[\Delta\text{-Ru}(\text{III})(\text{acac})_2(\text{taet})\}_3 \Delta\text{-Al}(\text{III})]$ were theoretically calculated using the Gaussian 16 program(B.01) in IMS [27]. The VCD intensities were determined by the vibrational rotational strength and the magnetic dipole moments, which were calculated by the magnetic field perturbation (MFP) theory formulated using magnetic field gauge-invariant atomic orbitals. The calculated intensities were converted to Lorentzian bands with a 4 cm^{-1} half-width at half-height. Geometry optimization was performed at the DFT level (B3LYP functional with 6-31G(d,p)). The observed spectra were assigned on the basis of animations of the molecular vibration with Gauss view 6.0 (Gaussian Inc., Wallingford, CT, USA).

5. Conclusions

Through an approach of chiral tectonics, a tetranuclear metal complex with pseudo D_3 symmetry, $[\{\Delta\text{-Ru}(\text{III})(\text{acac})_2(\text{taet})\}_3 \text{Al}(\text{III})]$ or $[\{\Lambda\text{-Ru}(\text{III})(\text{acac})_2(\text{taet})\}_3 \text{Al}(\text{III})]$, was prepared. In the synthesis, three units of one-handed chiral tecton, $[\text{Ru}(\text{III})(\text{acac})_n(\text{taetH})_{3-n}]$ (acacH = acetylacetonate, taetH_2 = tetraacetylene, $n = 2$), were self-assembled around an Al(III) ion in a solution. By use of the vibrational circular dichroism at low temperature and the time-dependent electronic circular dichroism (ECD) methods, the absolute configuration around the central core of the complex was determined and the kinetic properties of epimerization around a labile central core of Al(III) were obtained. The results postulated a new strategy for creating a dynamical network of the metal complex whose chirality is controlled in response to the stacking states.

Author Contributions: Conceptualization, Methodology, A.Y.; DFT calculation, H.S.; Investigation, H.S., F.S., and A.Y.; Writing-Original Draft Preparation, H.S.; Writing-Review & Editing, A.Y.

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