

Stereoselective Enhancement of VCD Signals for Intercalation Compounds of Sodium Montmorillonite and Chiral Metal Complexes

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Abstract

Vibrational circular dichroism (VCD) spectra were recorded for the intercalation compounds of sodium montmorillonite co-adsorbing two kinds of metal complexes, Δ - (or Λ -)[Ru-(phen)₃]²⁺ and Λ - (or Δ -)[Ni(phen)₃]²⁺. The complexes were chosen so as to form a pseudo racemate. Notably some of the VCD signals were enhanced in comparison to the samples adsorbing each complex separately. The results were rationalized in terms of the delocalization of vibrational motions over a tightly bound molecular pair in a coherent way. The model of racemic adsorption of [M(II)(phen)₃]²⁺ (M(II) = a divalent metal ion) in the interlayer space of a clay mineral was proposed.

Keywords:	Vibrational circular dichroism	
	Signal enhancement Clay minerals	

1. Introduction

Vibrational circular dichroism (VCD) spectroscopy is an extension of circular dichroism into the infrared region.^{1–7} The method is useful to determine the absolute configuration of a chiral molecule in a non-crystalline state. The detailed molecular conformation of a chiral molecule is deduced through the normal mode analysis of VCD peaks. In spite of such unique

advantages, however, the scope of its application is limited mostly to a stable molecule in a solution because of the extremely weak intensity of VCD signals. In order to overcome the difficulty, there have been several attempts realizing the enhancement of VCD signals. One example is a supramolecular aggregate under stereoregular ordering such as gels formed by chiral low molecular weight gelators.^{2,8} VCD signals are remarkably enhanced due to the gelators vibrating coherently over a long range along a helical fibril.

Recently the application of the VCD method was extended to solid materials.^{9–18} For example, we measured the VCD spectra of clay intercalation compounds.^{14–17} Sodium montmorillonite was ion-exchanged with a chiral metal complex, Δ or Λ -[Ru(phen)₃]²⁺ (phen = 1, 10-phenanthroline). Thereafter a chiral organic molecule, *R*- or *S*-2, 2'-binaphthol, was adsorbed as a target molecule whose chirality was discriminated by the pre-adsorbed metal complex.¹⁴ VCD spectra were proved to be dependent on the chirality relation between the discriminator and the target. With the help of theoretical simulations, the model was presented to show how they interacted in a stereoselective way on a clay surface.^{14,15}

In this work, we measured the VCD spectra of an intercalation compound of sodium montmorillonite co-adsorbing two kinds of metal complexes, Δ - (or Λ -)[Ru(phen)₃]²⁺ (phen = 1, 10-phenanthroline) and Λ - (or Δ -)[Ni(phen)₃]²⁺. The pair was chosen to form a pseudo racemate. The work was motivated by the previous finding on the adsorption properties of a smectite clay.^{19–24} When [M(II)(phen)₃]²⁺ (M(II) = a divalent metal ion) was adsorbed as a racemic mixture, it was

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adsorbed in two fold excess over the cation-exchange capacity (CEC) of a clay mineral. Δ - or Λ -[M(II)(phen)₃]²⁺ was adsorbed within the CEC when it was added as a pure enantiomer.²⁰ The facts were rationalized in terms of the tendency that racemic [M(II)(phen)₃]²⁺ formed a tight molecular pair on a clay surface, while enantiomeric [M(II)(phen)₃]²⁺ was located less densely due to steric interference.²² The detailed adsorption structures, however, remained to be established in spite of the extensive work by use of various spectroscopic means and theoretical simulation.^{24–27}

The present work applied the VCD method to reveal the intermolecular interactions between Δ - (or Λ -)[Ru(phen)₃]²⁺ and Λ - (or Δ -)[Ni(phen)₃]²⁺ within a clay mineral. It was intended to detect any change of VCD signals particularly when these two molecules co-existed in the interlayer space. As a result, some VCD signals were enhanced remarkably in comparison to the samples adsorbing each complex separately. The stacking structures were deduced by analysing the VCD spectra. The VCD measurements were further performed on the clay samples containing enantiopure [Ni(phen)₃]²⁺ and racemic [Fe(phen)₃]²⁺. A possibility was pursued that labile [Fe-(phen)₃]²⁺ might anti-racemize under the steric control of its neighbours. Based on the results, a model of molecular arrangement within an interlayer space was proposed.

2. Experimental

Sample Preparation. Enantiopure $[M(II)(phen)_3]SO_4$ (M(II) = Ru(II), Ni(II) and Fe(II)) were obtained as described previously.¹⁴ Sodium montmorillonite (Kunipia-F) was purchased from Kunimine Ind. Co. (Japan) (denoted by Na-MONT). The elemental composition and cation-exchange capacity (CEC) were stated to be (Na_{0.44}Ca_{0.03}) [(Al_{1.56}Mg_{0.32}-Fe_{0.10}Ti_{0.01})(Si_{3.85}Al_{0.15})O₁₀(OH)_{1.98}F_{0.02}] and 1.18 milliequivalents per gram, respectively.

An ion-exchange adduct of Na-MONT with Δ - (or Λ -)- $[Ru(phen)_3]^{2+}$ (denoted as Δ - (or Λ -) $[Ru(phen)_3]^{2+}/MONT$) was prepared as described previously. An ion-exchange adduct of Na-MONT with Δ - (or Λ -)[M(II)(phen)₃]²⁺ (denoted as Δ -(or Λ -)[M(II)(phen)₃]²⁺/MONT) (M(II) = Ni(II) and Fe(II)) was prepared in the same way except that the suspension was kept below 4 °C in order to prevent the racemization. In these samples, the metal complexes were adsorbed as divalent ions to more than 95% of the CEC of Na-MONT. A sample simultaneously containing two kinds of metal complexes (denoted as Δ - (or Λ -)[Ni(phen)₃]²⁺/ Λ - (or Δ -) [Ru(phen)₃]²⁺/MONT) was prepared by pouring an aqueous solution containing Λ - (or Δ -)[Ni(phen)₃]SO₄ into an aqueous suspension containing Δ -(or Λ -)[Ru(phen)₃]²⁺/MONT. After centrifuging the suspensions, the precipitates were dried under air at room temperature. A sample denoted as Δ - (or Λ -)[Ni(phen)₃]²⁺/racemic-[Fe(phen)₃]²⁺/MONT was prepared by pouring an aqueous solution containing racemic [Fe(phen)₃]SO₄ into an aqueous suspension containing Δ - (or Λ -)[Ni(phen)₃]²⁺/MONT. Both the poured solution and the clay dispersion were kept below 4 °C. After centrifuging, the solid residues of Δ - (or Λ -)- $[Ni(phen)_3]^{2+}/\Lambda$ - (or Δ -) $[Ru(phen)_3]^{2+}/MONT$ or Δ - (or Λ -)- $[Ni(phen)_3]^{2+}/racemic-[Fe(phen)_3]^{2+}/MONT$ were freezedried and mixed with dry KBr at ca. 1.5 wt % for the VCD measurements. The adsorption amounts of added metal complexes were obtained from measuring the electronic spectra of the filtrates. For Δ - (or Λ -)[Ni(phen)₃]²⁺/ Λ - (or Δ -) [Ru(phen)₃]²⁺/MONT, the adsorbed amounts of [Ru(phen)₃]²⁺ and [Ni(phen)₃]²⁺ were calculated to be ca. 95% and ca. 85% in terms of the CEC of MONT. For Δ - (or Λ -)[Ni(phen)₃]²⁺/ racemic-[Fe(phen)₃]²⁺/MONT, the adsorbed amounts of [Ni-(phen)₃]²⁺ and [Fe(phen)₃]²⁺ were calculated to be ca. 95% and ca. 75% in terms of the CEC of MONT. The excess amounts adsorbed over the CEC might be compensated by the adsorption of sulphate ions. As elucidated previously, no excess adsorption took place for a pseudo enantiomeric pair. That is, when Δ - (or Λ -)[Ni(phen)₃]SO₄ was added to an aqueous suspension containing Δ - (or Λ -)[Ru(phen)₃]²⁺/MONT, excess adsorption by Ni(II) chelates occurred to a negligible extent.

PXRD Measurements. X-ray powder diffraction measurements (PXRD) were performed with an XRD instrument (SmartLab SE and Ultima IV, Rigaku) under CuK α radiation ($\lambda = 0.15418$ nm) at 40 kV, 50 mA(or 40 mA), and 5°/min scanning.

VCD Measurements. VCD spectra were measured using a machine developed in house with the cooperation of JASCO Corporation, Japan (MultiD-MIRAI-2020 spectrometer).¹⁸ The machine was a concurrent system combined with QCL-VCD (quantum cascade laser) covering the wavenumber range of 1500–1740 cm⁻¹ and FT-VCD covering 800–2000 cm⁻¹. In this study, the samples were measured in the FT-VCD mode, using a normal cell holder under normal positioning. A sample was prepared by mixing an intercalation compound and dry KBr at 1.5 wt % and pressed to a disc of 10 mm ϕ in diameter. The resolution wavenumber was 4 cm⁻¹. The sample cell rotated along the direction of monitoring at 0 and 45 degree to confirm no interference from linear dichroism. The signals were accumulated over 10000 times. No baseline correction was made for all samples.

Computational Details. The IR and VCD spectra of the complexes were theoretically calculated using the Gaussian 16 program (C.01).²⁸ Geometry optimization was performed at the DFT level, in which B3LYP functional with Stuttgart ECP was employed for Ni(II), Ru(II), Fe(II) and 6-31G(d,p) for the other atoms, respectively. In the case of the molecular associate consisting of two metal complexes and one SO_4^{2-} ion, geometry optimization was performed at the DFT-d3 level. The VCD intensities were determined from the vibrational rotational strength and the magnetic dipole moments, which were calculated using the magnetic field perturbation theory formulated using magnetic field gauge-invariant atomic orbitals. The calculated intensities were converted to Lorentzian bands with a half-width of 4 cm^{-1} at half-height. The observed spectra were assigned based on the animations of the molecular vibration with Gaussview 6.0 (Gaussian Inc.).

3. Results and Discussion

PXRD Patterns of Intercalation Compounds. The following compounds were prepared and their PXRD patterns were obtained: Λ -[Ni(phen)₃]²⁺/MONT, Δ -[Ni(phen)₃]²⁺/MONT, Δ -[Ni(phen)₃]²⁺/ Δ -[Ru(phen)₃]²⁺/ Δ -[Ru(phen)₃]²⁺/ Δ -[Ru(phen)₃]²⁺/ Δ -[Ru(phen)₃]²⁺/ Δ -[Ni(phen)₃]²⁺/racemic-[Fe(phen)₃]²⁺/MONT and Δ -[Ni(phen)₃]²⁺/racemic-[Fe (phen)₃]²⁺/MONT. Figure 1 shows the selected PXRD



Figure 1. Powder X-ray diffraction patterns of clay intercalation compounds: (a) Λ -[Ni(phen)₃]²⁺/MONT (b) Δ -[Ni(II)(phen)₃]²⁺/ Λ -[Ru(phen)₃]²⁺/MONT (c) Λ -[Ni(II)-(phen)₃]²⁺/racemic-[Fe(phen)₃]²⁺/MONT.

patterns of these samples. The diffraction peak at the lowest diffraction angle corresponds to the basal spacing (denoted as d(001)) of montmorillonite layers. The height of an interlayer space (h) was calculated by subtracting the thickness of one layer (or 0.95 nm) from d(001) value.¹⁴ In the previous report, in case of Λ -[Ru(phen)₃]²⁺/MONT, the interlayer space was expanded from 1.24 nm to 1.73 nm.¹⁴ In case of A-[Ni- $(phen)_3$ ²⁺/MONT, the interlayer space was expanded to 1.80 nm as estimated from the peak at $2\theta = 4.90^{\circ}$ due to the replacement of sodium ions with $[Ni(phen)_3]^{2+}$ ions. The value of **h** was calculated to be 0.85 nm, which was nearly equal to the molecular height of $[Ni(phen)_3]^{2+}$ along its C_3 axis. Thus the Ni(II) chelate formed a monomolecular layer in the interlayer space. In the case of Δ -[Ni(phen)₃]²⁺/ Λ -[Ru(phen)₃]²⁺/ MONT, a new peak appeared at $2\theta = 3.25^{\circ}$ (or 2.72 nm) as d(001). The value of **h** was calculated to be 1.77 nm, indicating a bimolecular layer was formed. An external SO₄²⁻ ion might be located between the upper and lower molecular layers.²⁶ In the case of Λ -[Ni(phen)₃]²⁺/racemic-[Fe(phen)₃]²⁺/MONT a new peak appeared at $2\theta = 3.51^{\circ}$ (or 2.52 nm) in addition to the peak at $2\theta = 5.99^{\circ}$ (or 1.48 nm). The results indicated that the samples were a mixture of intercalation compounds with monomolecular and bimolecular layers. Thus the co-adsorption of $[Fe(phen)_3]^{2+}$ caused partially the further expansion of an interlayer space as seen for Δ - (or Δ -)[Ni(phen)₃]²⁺/ Λ - (or Δ -)- $[Ru(phen)_3]^{2+}/MONT$ samples.

IR and VCD Spectra of Intercalation Compounds. Black and red curves in Figure 2(a) show the IR (lower) and VCD (upper) spectra of Λ -[Ni(phen)³]²⁺/MONT and Δ -[Ni(phen)₃]²⁺/MONT, respectively. Two curves obeyed a mirror image relation as expected for the antipodal relation of the samples. The main peaks are indicated by alphabet, **a'**, **a**, **b**, **b'**, **c** and **c'**. When the spectrum for Λ -[Ni(phen)³]²⁺/MONT was compared with the theoretical simulation (Figure 2(b)), reasonable agreement was obtained for both IR and VCD results. Based on the results, main peaks were assigned as given in the supporting data (Table S1). The observed IR and VCD



Figure 2. (a) Observed IR (lower) and VCD (upper) spectra of the KBr pellets of clay intercalation compounds containing $[Ni(II)(phen)_3]^{2+}$: Λ - $[Ni(II)(phen)^3]^{2+}/MONT$ (black line) and Δ -[Ni(II)(phen)₃]²⁺/MONT (red line) (b) calculated IR (lower) and VCD (upper) spectra of A- $[Ni(II)(phen)_3]^{2+}$ (c) the pair with the opposite chirality: Λ -[Ni(II)(phen)₃]²⁺/ Δ -[Ru(phen)₃]²⁺/MONT (black line) Δ -[Ni(II)(phen)₃]²⁺/ Λ -[Ru(phen)₃]²⁺/MONT(red and line), respectively. No baseline correction was made. The number and alphabet are assigned for $[Ru(phen)_3]^{2+}/$ MONT and [Ni(II)(phen)₃]²⁺/MONT, respectively. [Ru- $(phen)_3$ ²⁺/MONT are shown in the supporting information (Figure S1). (d) Optimized structure of Λ -[Ru(phen)₃]²⁺ and Δ -[Ni(phen)₃]²⁺ with SO₄²⁻ ion; (e) Calculated IR (lower) and VCD (upper) spectra of Λ -[Ru(phen)₃]²⁺ and Δ -[Ni(phen)₃]²⁺ with SO₄²⁻ ion.

spectra of Λ - or Δ -[Ru(phen)³]²⁺/MONT were reported previously¹⁴ and are shown in the supporting data (Figure S1).

Black and red curves in Figure 2(c) show the IR (lower) and

VCD (upper) spectra of $\Lambda/[Ni(phen)_3]^{2+}/\Delta-[Ru(phen)_3]^{2+}/$ MONT and Δ -[Ni(phen)₃]²⁺/ Λ -[Ru(phen)₃]²⁺/MONT, respectively. There was little difference in the IR spectra between Figures 2(a) and (c). It implied that two intercalated complexes, $[Ni(phen)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$, are hardly discriminated from their IR spectra alone. In contrast, the VCD spectra had distinctive peaks assigned to either of the components. Thus the replacement of a central metal ion in $[M(II)(phen)_3]^{2+}$ resulted in the significant difference of its VCD spectra. Similar situations were noted previously for [M(III)(acac)₃].¹⁵ For this kind of a complex, the position and even sign of a VCD peak was influenced by the kind of a central metal ion. In Figure 2(c), the peaks assigned to $[Ni(phen)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$ are indicated by alphabet or number, respectively. These peaks are mainly assigned to the out-of-phase vibrations of phen ligands.^{14,29} They were mostly the overlap of the peaks in Figure 2(a) and Figure S1. In other words, both complexes underwent little structural change when they were adsorbed separately or simultaneously by Na-MONT.

It was noted that VCD peaks indicated by **a** and **b** in Figure 2(c) are enhanced in comparison to those in Figure 2(a). For example, the ratio of $\Delta A/A$ was calculated to be 1.8 times higher for Δ - (or Λ -) [Ni(phen)₃]²⁺/ Λ - (or Δ -)[Ru(phen)₃]²⁺/MONT than that for Δ - (or Λ -)[Ni(phen)₃]²⁺/MONT. Enhancement was also recognized for **1'** assigned to [Ru(phen)₃]²⁺.

According to the previous analyses on the enhancement of a VCD signal, the main cause was sought in the delocalization of vibrational motions over a tightly bound molecular associate.¹⁴ In the case of metal complexes, the vibrational delocalization took place when they were stacked with their ligands faced closely. Thus it was concluded that, in the present case, $[Ni(phen)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ were stacked in Δ - (or Λ -) $[Ni(phen)_3]^{2+}/\Lambda$ - (or Δ -) $[Ru(phen)_3]^{2+}/MONT$, while no such close stacking occurred in Δ - (or Λ -) $[Ni(phen)_3]^{2+}/MONT$ or Δ - (or Λ -) $[Ru(phen)_3]^{2+}/MONT$.

In order to study the details of vibrational delocalization, a theoretical calculation was carried out for a pair of A-[Ru- $(\text{phen})_3$ ²⁺ and Δ -[Ni(phen)₃]²⁺. Figure 2(d) is the optimized structure of the ternary system of Λ -[Ru(phen)₃]²⁺, Δ -[Ni- $(phen)_3]^{2+}$ and SO_4^{2-} , in which SO_4^{2-} is included as an external anion in the bimolecular layer. The interatomic distance between Ru(II) and Ni(II) is estimated to be 1.01 nm. Figure 2(e) shows the IR (lower) and VCD spectra (upper) calculated for such an associate. It is predicted that the peak at $1630 \,\mathrm{cm}^{-1}$, which corresponds to peak a in Figure 2(c), is assigned to C-C-C stretching vibration of phen ligands in Δ -[Ni(phen)₃]²⁺. According to the calculation, the vibrational motion at the peak is coherently accompanied with the C-C stretching vibration of the two phen ligands in Λ -[Ru(phen)₃]²⁺. In a similar way, the peak at 1464 cm⁻¹, which corresponds to peak c in Figure 2(c), is assigned to the overlap of C-C-C stretching and C-H bending of phen in Λ -[Ru(phen)₃]²⁺. The motion is also accompanied with the vibrations in the two phen ligands in Δ -[Ni(phen)₃]²⁺.

Red and black curves in Figure 3(a) show the IR (lower) and VCD (upper) spectra of Λ -[Fe(phen)³]²⁺/MONT and Δ -[Fe(phen)₃]²⁺/MONT, respectively. The main peaks are indicated by **I**, **I'**, **II**, **II'**, **III** and **III'**. The curves roughly obeyed a mirror image relation as expected for the antipodal pair, although the occurrence of the partial racemization of labile



Figure 3. Observed IR (lower) and VCD (upper) spectra of KBr pellets of clay intercalation compounds containing $[Fe(phen)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$: (a) Λ - $[Fe(phen)_3]^{2+}/MONT$ (red) and Δ - $[Fe(phen)_3]^{2+}/MONT$ (black); (b) Λ - $[Ni(II)(phen)_3]^{2+}/racemic-[Fe(phen)_3]^{2+}/MONT$ (black) and Δ - $[Ni(II)(phen)_3]^{2+}/racemic-[Fe(phen)_3]^{2+}/MONT$ (red), respectively. No baseline correction was made. The Roman numbers and alphabet indicate the peaks assigned to $[Fe(phen)_3]^{2+}$ and to $[Ni(phen)_3]^{2+}$, respectively. Two asterisks, * and **, denote the enhanced VCD peaks assigned to $[Fe(phen)_3]^{2+}$, and co-existing $[Ni-(phen)_3]^{2+}$, respectively.

 Δ - or Λ -[Fe(phen)³]²⁺ during the intercalation process might lower the intensity of VCD signals.

Black and red curves in Figure 3(b) show the IR (lower) and VCD (upper) spectra of Λ -[Ni(phen)₃]²⁺/racemic-[Fe- $(phen)_3$ ²⁺/MONT and Δ -[Ni(phen)₃]²⁺/racemic-[Fe- $(phen)_3$ ²⁺/MONT, respectively. It was noted that there were VCD peaks assigned either to Λ -[Fe(phen)₃]²⁺ or to Δ - $[Fe(phen)_3]^{2+}$ observed in the samples of Λ - $[Ni(phen)_3]^{2+}/$ racemic-[Fe(phen)₃]²⁺/MONT and Δ -[Ni(phen)₃]²⁺/racemic-[Fe(phen)₃]²⁺/MONT, respectively. The appearance of VCD peaks assigned to [Fe(phen)₃]²⁺ was clear evidence that [Fe- $(phen)_3$ ²⁺ anti-racemized to be enriched to either enantiomer when it was co-adsorbed with enantiopure $[Ni(phen)_3]^{2+}$. Moreover, peaks II and III assigned to $[Fe(phen)_3]^{2+}$ decreased their intensity in comparison to the samples containing enantiopure $[Fe(phen)_3]^{2+}$ alone (Figure 3(a)). This was caused by the cancellation by the peaks assigned to coexisting $[Ni(phen)_3]^{2+}$ with antipodal configuration. It should be noted that racemic $[Fe(phen)_3]^{2+}$ was anti-racemized to Δ - $[Fe(phen)_3]^{2+}$ or to Λ - $[Fe(phen)_3]^{2+}$ in Λ - $[Ni(phen)_3]^{2+}$ /racemic- $[Fe(phen)_3]^{2+}$ / MONT or Δ -[Ni(phen)₃]²⁺/racemic-[Fe(phen)₃]²⁺/MONT, respectively. Thus the conversion was driven by the tendency that labile $[Fe(phen)_3]^{2+}$ preferred to form a pseudo-racemic pair with pre-adsorbed [Ni(phen)₃]²⁺.

The above anti-racemization was previously proposed for a colloidal dispersion of Na-MONT containing enantiopure $[Ni(phen)_3]^{2+}$ and racemic $[Fe(phen)_3]^{2+}$.¹⁹ On the basis of the induction of a new peak in VCD spectra, $[Fe(phen)_3]^{2+}$ was proposed to anti-racemize on a clay surface. The present VCD experiments supported the conclusions. The detailed analyses



Figure 4. Models proposed for molecular arrangement in bimolecular layer: (a) (**Model 1**) one layer consists of Δ -enantiomers and that the other of Λ -enantiomers; (b) (**Model 2**) one layer contains Δ - and Λ -enantiomers at 2:1 ratio in hexagonal arrangement and that the other at 1:2. Green and blue circles represent such as Λ -[Ru(phen)₃]²⁺ and Δ -[Ni(phen)₃]²⁺, respectively.

of the VCD spectra are given in the supporting information together with the comparison of the VCD spectra of Λ -[Fe(phen)₃]²⁺ with the theoretical calculation (Figures S2–S4 and Table S2).

A Model Proposed for Racemic Adsorption. The layer surface of a smectite clay mineral consists of the phyllosilicate sheets of smectite layer. It is characterized by the two-dimensional lattice of hexagonal holes made by $[SiO_4]^{4-}$ tetrahedrons.^{30–32} When $[M(II)(phen)_3]^{2+}$ is adsorbed onto the surface, the molecule orients with its C_3 axis perpendicularly to satisfy the geometrical matching between its three-bladed propeller and a lattice of hexagonal holes.²⁴ Under the conformation, interaction energy depends remarkably whether a neighboring pair is enantiomeric or racemic.^{19,20} The situations are considered to be a main factor leading to the occurrence of excess adsorption for a racemic mixture. The properties made a clay mineral ion-exchanged with enantiopure $[M(II)(phen)_3]^{2+}$ an efficient chiral discriminator.^{20–24}

Very recently the two-dimensional X-ray diffraction measurements were performed on the samples of racemic [Ni-(phen)₃]²⁺/MONT.²⁷ The presence of the two-dimensional periodicity was confirmed in the bimolecular adsorption layer. In order to rationalize the results, two models are presented for explaining the experimental results. The first model is that two homochiral layers consisting of either Δ - and Λ -enantiomers are overlapped (**Model 1**). The second model is the overlap of two heterochiral layers, each of which consists of the hexagonal arrangement of Δ - and Λ -enantiomers at either 2:1 or 1:2 ratio. In one layer, a Δ - (or Λ -) enantiomer is surrounded by six Λ - (or Δ -) enantiomers (**Model 2**). These two models are schematically shown in Figures 4(a) and (b).

The present results obtained by VCD measurements demonstrated that pseudo racemic pair between Δ - (or Λ -)[Ru-(phen)₃]²⁺ and Λ - (or Δ -)[Ni(phen)₃]²⁺ formed a compact associate in which the components are stacked so closely to realize coherent vibrational motions. Such a compact pair would be formed more readily in case of **Model 2**, since a Δ -[M(II)(phen)₃]²⁺ ion is surrounded by six Λ -[M(II)(phen)₃]²⁺ ions in the same monomolecular layer. In case of **Model 1**, the tight association between Δ -[M(II)(phen)₃]²⁺ and Λ -[M(II)-(phen)₃]²⁺ ions would be more difficult since they are located in the different monomolecular layers. Moreover, according to **Model 2**, a labile [Fe(phen)₃]²⁺ ion was surrounded by six enantiopure [Ni(phen)₃]²⁺ ions in the samples of Λ - or Δ - $[Ni(phen)_3]^{2+}/racemic-[Fe(phen)_3]^{2+}/MONT.$ Under the steric control by $[Ni(phen)_3]^{2+}$ ions, $[Fe(phen)_3]^{2+}$ would be antiracemized to an enantiomer antipodal to the surrounding $[Ni(phen)_3]^{2+}$ ions. It would be interesting to measure the VCD spectra of montmorillonite samples containing two different kinds of enantiopure $[M(II)(phen)_3]^{2+}$ at 2:1 or 1:2 ratio.

4. Conclusion

A 1:1 mixture of Δ - (or Λ -)[Ru(phen)₃]²⁺ and Λ - (or Δ -)-[Ni(phen)₃]²⁺ was adsorbed by sodium montmorillonite to form a bimolecular layer in the interlayer space. The solid state VCD spectroscopy was applied to reveal the details of molecular arrangement within the layer. The metal complexes were concluded to form a tightly stacked pair from the appearance of the enhanced VCD peaks. The present results supported a model of molecular arrangement proposed in which Δ - and Λ -enantiomers form a two-dimensional hexagonal lattice at a 1:2 or 2:1 ratio on the surface of a clay mineral. The VCD method was proved to be efficient for revealing microscopic molecular organization within a solid host material.

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Supporting Information

Assignment of calculated VCD peaks for Λ -[Ni(phen)₃]²⁺; experimental VCD and IR spectra of Δ - and Λ -[Ru(phen)₃]²⁺/ montmorillonite; calculated VCD and IR spectra of Λ -[Fe(phen)₃]²⁺; optimized structure of the ternary system of Δ -[Ni(phen)₃]²⁺, Λ -[Fe(phen)₃]²⁺ and SO₄²⁻; calculated IR and VCD spectra for the ternary system involving Δ -[Ni(phen)₃]²⁺, Λ -[Fe(phen)₃]²⁺ and SO₄²⁻. This material is available on https://doi.org/10.1246/bcsj.20210101.

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