Inorg. Chem. **1985**, *24*, 1689–1695

Table II. Comparison between Models for the Chloro Complex Formation of Ga(III) in KCl–$AlCl_3$ Melts at 300 °C[a] (0.1 F $GaCl_3$ Solutions)

model no.	equilibria	p*K*	variance × 10^5
1	$GaCl_4^- \rightleftharpoons GaCl_3 + Cl^-$	6.02 ± 0.03	2.0*
2	$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^-$	4.20 ± 0.10	2.6*
3	$2GaCl_4^- \rightleftharpoons Ga_2Cl_6 + 2Cl^-$	10.88 ± 0.07	5.9
4	$3GaCl_4^- \rightleftharpoons Ga_3Cl_{10}^- + 2Cl^-$	9.17 ± 0.09	1.6*
5	$GaCl_4^- + AlCl_4^- \rightleftharpoons GaAlCl_7^- + Cl^-$	6.74 ± 0.03	1.2*
6	$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^-$	4.97 ± 0.19	
	$Ga_2Cl_7^- \rightleftharpoons 2GaCl_3 + Cl^-$	7.3 ± 0.3	1.3*
7	$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^-$	4.59 ± 0.11	
	$Ga_2Cl_7^- \rightleftharpoons Ga_2Cl_6 + Cl^-$	6.39 ± 0.11	1.2*
8	$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^-$	4.60 ± 0.11	
	$3Ga_2Cl_7^- \rightleftharpoons 2Ga_3Cl_{10}^- + Cl^-$	4.78 ± 0.16	1.6*
9	$3GaCl_4^- \rightleftharpoons Ga_3Cl_{10}^- + 2Cl^-$	13.4 ± 0.03	
	$Ga_3Cl_{10}^- \rightleftharpoons 3GaCl_3 + Cl^-$	4.6 ± 0.3	2.3*
10	$3GaCl_4^- \rightleftharpoons Ga_3Cl_{10}^- + 2Cl^-$	9.21 ± 0.09	
	$2Ga_3Cl_{10}^- \rightleftharpoons 3Ga_2Cl_6 + 2Cl^-$	18.4 ± 1.0	1.9*
11	$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^-$	6.56 ± 0.11	
	$GaCl_4^- + AlCl_4^- \rightleftharpoons GaAlCl_7^- + Cl^-$	6.78 ± 0.04	1.2*

[a] 0.1 M $GaCl_3$ solutions. Asterisks are based on $F_{0.10}(7.4) = 3.98$ (one equilibrium) or $F_{0.10}(6.4) = 4.01$ (two equilibria).

For each model the best p*K* value (i.e. the one that gave the lowest variance) was found by a computer program. The potassium chloride formality was least-squares fitted by means of Marquardt's method for nonlinear regression[22] using the p*K* values as independent variables. By comparison of the so obtained minimum variances for each model with the experimental variance, an *F* test can be used to make distinction between models with more or less probability than 90%.

In Table II the results of the calculations on models involving such complexes are shown. Models with a probability of more than 90% compared with the experimental variance are marked with an asterisk.

When only one equilibrium is taken into account, the potentiometric measurements can be explained by several models. The lowest variance is, however, obtained for the formation of the mixed Ga(III)–Al(III) complex $GaAlCl_7^-$ according to the equation

$$GaCl_4^- + AlCl_4^- \rightleftharpoons GaAlCl_7^- + Cl^- \qquad (5)$$

If three Ga(III)–chloride complexes are supposed to exist, the calculations show that models involving $Ga_2Cl_7^-$ (i.e. eq 1 as the first equilibrium) generally have small variances. Two different possibilities for the third Ga(III) species give the minimum variance, namely Ga_2Cl_6 and $GaAlCl_7^-$. Since the Raman spectroscopic measurements suggested that a mixed Ga(III)–Al(III) chloro complex was present in acidic solutions of $GaCl_3$ in KCl–$AlCl_3$, it seems likely that $GaAlCl_7^-$ is the best choice for the third complex.

Acknowledgment. I wish to thank R. W. Berg and B. Christensen for assistance with the measurements and N. J. Bjerrum for valuable discussions. Further thanks are due to Statens teknisk-videnskabelige Forskningsråd for financial support.

Registry No. $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3; $GaAlCl_7^-$, 95156-16-4; $Ga_2Cl_7^-$, 33847-92-6; KCl, 7447-40-7.

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[22] Marquardt, D. W. IBM Share Library, Distribution No. 309401 (Aug 1966).

Contribution from the Faculty of Science,
Hokkaido University, Sapporo 060, Japan

Racemic Adsorption, Antiracemization, and Induction of Optical Activity of Metal Chelates in the Presence of a Colloidal Clay

AKIHIKO YAMAGISHI

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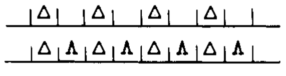
The adsorption of an optically active metal chelate by a colloidal particle of sodium–montmorillonite clay has been studied by means of the electronic spectra and electric dichroism and circular dichroism measurements. An adduct of a clay with Λ-tris(1,10-phenanthroline)ruthenium(II) (Λ-$Ru(phen)_3^{2+}$) accepted the adsorption of Δ-$M(phen)_3^{2+}$ (M = Ru, Fe, Ni) but not Λ-$M(phen)_3^{2+}$ in excess over the cation-exchange capacity. Due to such stereospecific adsorption, the racemic mixture of a labile metal complex such as $Co(phen)_3^{2+}$ and $Fe(phen)_3^{2+}$ antiracemized in the presence of Λ-$Ru(phen)_3^{2+}$–montmorillonite (or Δ-$Ni(phen)_3^{2+}$–montmorillonite). When an achiral molecule such as the acridine orange cation was adsorbed by Δ-$Ni(phen)_3^{2+}$–montmorillonite, the optical activity was induced in the electronic spectrum of the adsorbate.

Introduction

Recently I studied the adsorption of an optically active metal chelate by a colloidally dispersed clay.[1] Certain tris-chelated complexes were found to be adsorbed as a single unit of a racemic pair. For example, tris(1,10-phenanthroline)iron(II) ($Fe(phen)_3^{2+}$) was adsorbed within the cation-exchange capacity (CEC) of a clay when the chelate was added as a pure enantiomer. On the other hand, the same chelate was adsorbed in a 2-fold excess of the CEC from a solution of a racemic mixture. Schematically the states of saturated adsorptions of enantiomeric and racemic $Fe(phen)_3^{2+}$ can be written as (1) and (2), respectively. At a state (2), the closely stacked racemic pairs were distributed over a bidimensional surface of a silicate sheet of a clay. Such highly packed states were, however, impossible for enantiomeric adsorption (1) because of the steric interference between the adjacent molecules.



(1)
(2)

This paper describes the new aspects concerning the above phenomena. One is the study of the competitive adsorption of two different metal chelates on a colloidal clay. The results clarified to what extent the competitive chelates should possess structural similarity for realizing the highly packed state as in (2). The other is the antiracemization and induction of optical activity of a metal chelate when the molecule was adsorbed on an empty site of a clay surface at a state (1). The results revealed that a surface (1) not only recognized the absolute configuration of a new adsorbate but also stabilized the configuration of an adsorbed molecule against racemization. As a result, a labile metal complex, which was added to the system of a clay–optically active chelate adduct, was accumulated as a pure enantiomer.

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[1] (a) Yamagishi, A.; Soma, M. *J. Am. Chem. Soc.* **1981**, *103*, 4640. (b) Yamagishi, A. *J. Phys. Chem.* **1982**, *86*, 2472.

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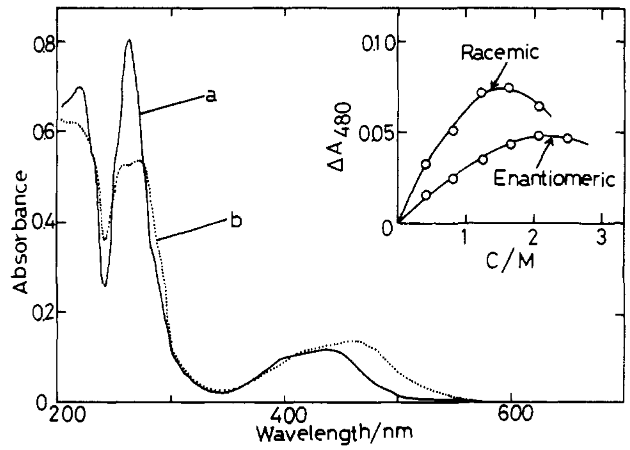

Figure 1. Electronic spectra of aqueous solutions of racemic Ru(phen)$_3$(ClO$_4$)$_2$: curve a, [Ru(phen)$_3$(ClO$_4$)$_2$] = 5 × 10^{-6} M; curve b, 3 × 10^{-6} M sodium-montmorillonite (Na$^+$-M$^-$) added to the first solution. The inset is the plot of the absorbance change at 480 nm against the ratio of Na$^+$-M$^-$ to Ru(phen)$_3^{2+}$ (*C*/*M*).

Experimental Section

Materials. Sodium-montmorillonite (Na$^+$-M$^-$) was purchased from Kunimine Ind. Co. Ltd. (Tokyo, Japan). The stated cation-exchange capacity (CEC) was 115 mequiv/100 g. In preparing a sample solution, about 1 g of Na$^+$-M$^-$ was dispersed in 100 mL of deionized water. The solution was centrifuged at 5000 rps, and the supernatant solution was filtered through a membrane filter (Toyo, Tokyo, Japan) with a maximum passage of 0.45 μm. The filtrate contained about 20 mg/100 mL of clay. The CEC of the stock solution was determined spectrophotometrically by use of the adsorption of acridine orange hydrochloride.[2]

Optically active Ru(phen)$_3$(ClO$_4$)$_2$ was synthesized according to the literature method.[3] Optically active perchlorate salts of Ni(phen)$_3^{2+}$, Fe(phen)$_3^{2+}$, and Co(en)$_3^{3+}$ (en = ethylenediamine) were prepared by the conventional methods.[4] Λ-Co(phen)$_3$(ClO$_4$)$_3$ was synthesized according to the method of Lee et al.[5] Racemic mixtures of Co(phen)$_3^{2+}$, Fe(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridyl), Fe(batho)$_3^{2+}$ (batho = bathophenanthroline), Fe(batho-SO$_3$)$_3^{4-}$ (batho-SO$_3$ = bathophenanthrolinedisulfonato), and M(PAN)$_2$ (PAN = 1-(2-pyridylazo)-2-naphthol) were prepared by mixing the corresponding ligands and perchlorate salts of divalent metal ions. N-Alkylated acridine orange cations were synthesized as described elsewhere.[6]

Instruments. Electronic spectra were recorded on a Hitachi EPS-3T spectrophotometer at 20 °C. Electric dichroism was measured with an instrument as described previously.[7] An electric field pulse with an intensity of 7.5 kV/cm and duration of 1 ms was generated with an electric field pulse generator (Denkenseiki, Tokyo, Japan). Circular dichroism spectra (CD spectra) were measured with a J-500A spectropolarimeter (JASCO, Tokyo, Japan) at room temperature. A cell with an optical length of 1 or 10 cm was used for the CD measurements as stated in the figure captions.

Results

(1) Electric Dichroism Studies on Adsorption of Metal Chelates by a Colloidal Clay. When two kinds of metal complexes were present in a colloidal clay solution, they would compete for occupation of the binding sites of a clay. Such competitive adsorptions were studied by means of electric dichroism measurements. The method enabled us to obtain the amounts of adsorbed complexes under conditions of very dilute concentrations (<10^{-4} M). The investigated system was a solution of Λ-Ru(phen)$_3^{2+}$-montmorillonite in the presence of another kind of metal complex.

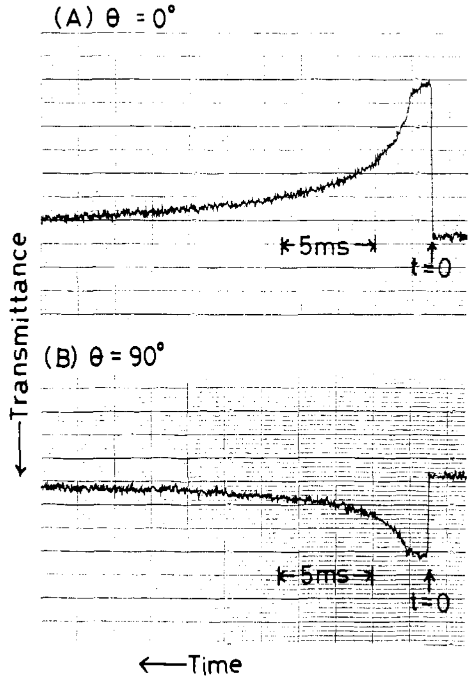

Figure 2. Electric dichroism signals for an aqueous solution of racemic Ru(phen)$_3$(ClO$_4$)$_2$ and a clay. The monitoring light at 450 nm was polarized (A) in parallel with (θ = 0°) or (B) vertical to (θ = 90°) the applied electric field. At *t* = 0, an electric field pulse with a duration of 1 ms was imposed on the solution.

Curve a in Figure 1 is the electronic spectrum of an aqueous solution of racemic Ru(phen)$_3^{2+}$. The absorption peak at 262 nm was attributed to the π-π* transitions of the phenanthroline ligands, while the broad band at 350-550 nm arose from the charge-transfer transitions from Ru^{2+} to the ligands.[8] When sodium-montmorillonite was added to the solution, the spectrum changed from curve a to curve b. The peak at 262 nm split to form two peaks with concomitant decrease of absorbance. The charge-transfer band in the visible region was displaced toward the longer wavelength. These spectral changes were caused by the adsorption of Ru(phen)$_3^{2+}$ by a colloidal particle of a clay. In order to obtain the stoichiometry of adsorption equilibrium, the absorbance change at 480 nm, ΔA_{480}, was plotted against the ratio of the CEC of an added clay to Ru(phen)$_3^{2+}$, *C*/*M*. In the case of Λ-Ru(phen)$_3^{2+}$, ΔA_{480} increased monotonically until it reached a maximum value of 0.05 at *C*/*M* = 2.2. Contrary to this, ΔA_{480} for racemic Ru(phen)$_3^{2+}$ increased more steeply until it attained the maximum value of 0.075 at *C*/*M* = 1.2. The results indicated that enantiomeric Ru(phen)$_3^{2+}$ was adsorbed by a clay and occupied about two cation-exchange sites per molecule, while racemic Ru(phen)$_3^{2+}$ was adsorbed by a clay and occupied approximately one cation-exchange site per molecule. At least it was certain that racemic Ru(phen)$_3^{2+}$ was bound to a clay in 2-fold excess of the adsorbed amount of enantiomeric Ru(phen)$_3^{2+}$. Thus the chelate was concluded to be adsorbed by a clay as a single unit of a racemic pair.

The electric dichroism was measured by imposing an electric field pulse on a solution of Ru(phen)$_3^{2+}$ and a colloidal clay. Figure 2 exhibits the electric dichroism signals for racemic Ru(phen)$_3^{2+}$ bound to a clay. The monitoring light was polarized parallel with (θ = 0°) or perpendicular to (θ = 90°) the electric field in Figure 2, part A or B, respectively. The stationary amplitudes of the signals obeyed the expression for orientational dichroism

$$\Delta A/A = (\rho/6)(1 + 3\cos 2\theta) \qquad (3)$$

in which $\Delta A/A$ is the relative absorbance change, θ the angle between an electric field and the polarization of a monitoring light, and ρ a reduced linear dichroism defined by $\rho = (\epsilon_{\parallel} - \epsilon_{\perp})/\epsilon$.[9] No

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[3] Gillard, R. D.; Hill, R. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1217.

[4] "New Treatise on Experimental Chemistry"; Maruzen: Tokyo, 1975; Vol. 8.

[5] Lee, C. S.; Gorton, E. M.; Neumann, H. M.; Hunt, H. R., Jr. *Inorg. Chem.* **1966**, *5*, 1397.

[6] Yamagishi, A.; Masui, T.; Watanabe, F., *J. Phys. Chem.* **1981**, *85*, 281.

[7] Yamagishi, A. *Biopolymers* **1981**, *20*, 201.

[8] McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1969**, 1428.

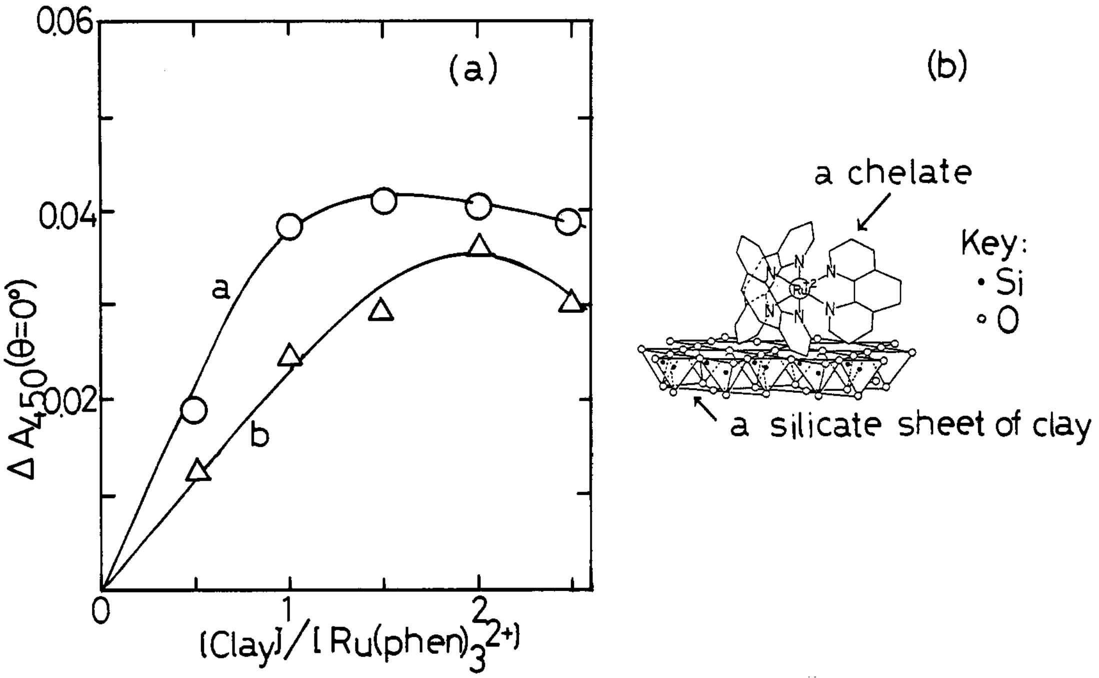

Figure 3. (a) Dependence of the amplitude of the electric dichroism signal at θ = 0° and 450 nm, $\Delta A_{450}(\theta = 0°)$, on the ratio of clay (Na$^+$–M$^-$) to Ru(phen)$_3$(ClO$_4$)$_2$: curve a (○), 6 × 10^{-6} M racemic Ru(phen)$_3^{2+}$; curve b (△), 6 × 10^{-6} M Λ-Ru(phen)$_3^{2+}$. Various amounts of Na$^+$–M$^-$ were added. (b) Proposed bound structure of Ru(phen)$_3^{2+}$.

dichroic change was observed when an electric field was applied on a solution of Ru(phen)$_3^{2+}$ alone. Thus the dichroism was induced by the orientation of Ru(phen)$_3^{2+}$ bound to a colloidal clay particle. A platelike particle of montmorillonite orientates under an electric field with its planar surface parallel with the field.[10]

Figure 3a shows the dependence of the stationary amplitude of the dichloism at θ = 0°, $\Delta A(\theta = 0°)$, on the ratio of clay to metal chelate, C/M. For racemic Ru(phen)$_3^{2+}$, $\Delta A(\theta = 0°)$ increased linearly until it reached a saturated value of 0.045 at C/M = 1.4. On the other hand, $\Delta A(\theta = 0°)$ for enantiomeric Ru(phen)$_3^{2+}$ increased less steeply until it became a maximum of 0.037 at C/M = 2.0. These results were coincided well with the previous spectroscopic ones, shown in Figure 1, indicating that $\Delta A(\theta = 0°)$ could be a measure of the adsorbed amount of Ru(phen)$_3^{2+}$ for both racemic and enantiomeric solutions. Saturated values of $\Delta A(\theta = 0°)$ corresponded to the dichroism amplitude when the whole of the added chelate was adsorbed by a clay. The reduced linear dichroism, ρ, in eq 3 was found to be 0.75 and 0.73 for racemic and enantiomeric Ru(phen)$_3^{2+}$, respectively. ρ was dependent on the orientation of the transition moment due to a bound chelate and also on the electric field strength (E). The transition moment of Ru(phen)$_3^{2+}$ in the visible region lies in a plane perpendicular to the C_3 axis of the chelate.[8] In such a case, ρ is given by

$$\rho = -\tfrac{3}{8}(1 + 3 \cos 2\varphi)\cdot\Phi(E) \qquad (4)$$

in which φ is the angle between an electric field and the C_3 axis and $\Phi(E)$ an orientation function representing the degree of orientation of a particle at given E.[11] $\Phi(E)$ takes a value of 0 at E = 0 and 1 at $E = \infty$.[9] ρ was measured in the range E = 7.5–24 kV·cm^{-1}. ρ was constant, indicating that a clay particle orientated completely under the present electric field strength ($\Phi(E)$ = 1). By insertion of the obtained ρ and $\Phi(E)$ = 1 into eq 4, φ was calculated to be 90 and 85° for racemic and enantiomeric adsorptions of Ru(phen)$_3^{2+}$, respectively. In other words, the chelate was bound to a clay with its C_3 axis perpendicular to the clay surface (Figure 3b).

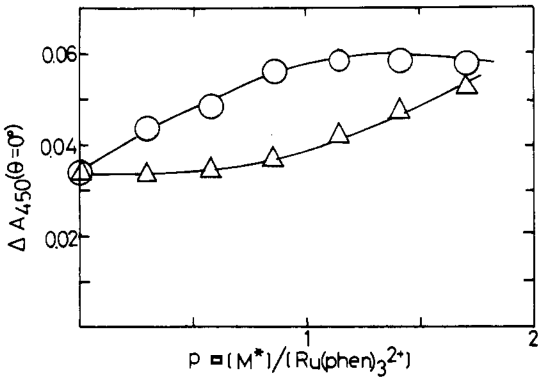

Figure 4. Plots of $\Delta A_{450}(\theta = 0°)$ for a solution of Λ-Ru(phen)$_3^{2+}$–montmorillonite against the ratio of newly added Ru(phen)$_3^{2+}$ to initially present Λ-Ru(phen)$_3^{2+}$ ([Λ-Ru(phen)$_3^{2+}$–montmorillonite] = 6 × 10^{-6} M): curve a (△), Λ-Ru(phen)$_3^{2+}$ added; curve b (○), Δ-Ru(phen)$_3^{2+}$ added.

In the following experiments, $\Delta A(\theta = 0°)$ was measured for a solution of Λ-Ru(phen)$_3^{2+}$–montmorillonite in the presence of another kind of metal chelate. $\Delta A(\theta = 0°)$ was plotted against the ratio p = [M*]/[Ru], in which [M*] and [Ru] denoted the concentrations of another kind of metal chelate and the initial Ru chelate, respectively. In the interpretation of the results, $\Delta A(\theta = 0°)$ was taken to be proportional to the amount of a bound chelate.

In Figure 4, either Λ-Ru(phen)$_3^{2+}$ or Δ-Ru(phen)$_3^{2+}$ was added to a solution of Λ-Ru(phen)$_3^{2+}$–montmorillonite. For M* = Λ-Ru(phen)$_2^{2+}$, $\Delta A(\theta = 0°)$ at 450 nm varied little below p = 1. $\Delta A(\theta = 0°)$ increased in the range p = 1–2. The results implied that Λ-Ru(phen)$_3^{2+}$–montmorillonite did not accept the further binding of the same enantiomer unless there existed a large excess of Λ-Ru(phen)$_3^{2+}$ in a solution. In the case of M* = Δ-Ru(phen)$_3^{2+}$, $\Delta A(\theta = 0°)$ increased linearly until it reached a saturated value at p = 1. This meant that Λ-Ru(phen)$_3$–montmorillonite adsorbed Δ-Ru(phen)$_3^{2+}$ in excess over the CEC of a clay. Therefore, the above results provided direct evidence for the fact

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(9) Dourlent, M.; Hogrel, J. F.; Helen, C. J. *J. Am. Chem. Soc.* **1974**, *96*, 3398. ϵ, $\epsilon_{\parallel}$, and $\epsilon_{\perp}$ denote the molar extinction coefficients for nonpolarized light and light polarized parallel with and perpendicular to the electric field, respectively.

(10) Shah, M. J.; Thompson, D. C.; Hart, C. M. *J. Phys. Chem.* **1963**, *67*, 1170.

(11) O'Konski, C. T.; Yoshioka, K.; Orttung, W. H. *J. Phys. Chem.* **1959**, *63*, 1558.

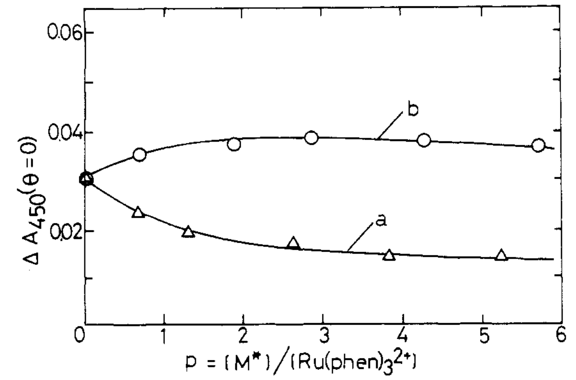

Figure 5. Plots of $\Delta A_{450}(\theta = 0^\circ)$ for a solution of Λ-Ru(phen)$_3^{2+}$–montmorillonite against the ratio of newly added Ni(phen)$_3^{2+}$ to initially present Λ-Ru(phen)$_3^{2+}$ ([Λ-Ru(phen)$_3^{2+}$–montmorillonite] = 6×10^{-6} M): curve a ($\triangle$), Λ-Ni(phen)$_3^{2+}$ added; curve b (○), Δ-Ni(phen)$_3^{2+}$ added.

that Ru(phen)$_3^{2+}$ was adsorbed by a clay as a unit of a racemic pair.

Curves a and b in Figure 5 exhibit similar plots for the Λ-Ru(phen)$_3^{2+}$–montmorillonite solution in the presence of the enantiomers of Ni(phen)$_3^{2+}$ as competitive ions. Since Ni(phen)$_3^{2+}$ negligibly absorbed visible light under the present concentration ($<10^{-4}$ M), $\Delta A(\theta = 0^\circ)$ arose exclusively from bound Λ-Ru(phen)$_3^{2+}$. For M* = Λ-Ni(phen)$_3^{2+}$, $\Delta A(\theta = 0^\circ)$ decreased gradually to a saturated value of 0.015 above $p = 5$ (curve a). The decrease of $\Delta A(\theta = 0^\circ)$ indicated that bound Λ-Ru(phen)$_3^{2+}$ ions were dissociated from a clay as they were replaced with Λ-Ni(phen)$_3^{2+}$ ions. In other words, Λ-Ni(phen)$_3^{2+}$ competed with Λ-Ru(phen)$_3^{2+}$ for the same binding sites on a clay. Notably $\Delta A(\theta = 0^\circ)$ did not become zero but some definite value at a large excess of Λ-Ni(phen)$_3^{2+}$. The results were interpreted by the assumption that a part of the Λ-Ru(phen)$_3^{2+}$ ions were attracted toward Λ-Ni(phen)$_3^{2+}$–montmorillonite in excess over the CEC of a clay. Most probably, there existed an attractive interaction between Λ-Ru(phen)$_3^{2+}$ and Λ-Ni(phen)$_3^{2+}$ on a clay surface due to the dispersive force of the phenanthroline ligands. When Δ-Ni(phen)$_3^{2+}$ was added, $\Delta A(\theta = 0^\circ)$ increased initially until it stayed at a constant value of 0.038 in the range $p = 1$–4 (curve b). This meant that Λ-Ru(phen)$_3^{2+}$ was not replaced with Δ-Ni(phen)$_3^{2+}$ but the latter was adsorbed by Λ-Ru(phen)$_3^{2+}$–montmorillonite in excess over the CEC of a clay. On a clay surface, a "pseudoracemic pair" was formed between Λ-Ru(phen)$_3^{2+}$ and Δ-Ni(phen)$_3^{2+}$. The initial small increase in $\Delta A(\theta = 0^\circ)$ might arise from the increase of absorption in the static spectrum of a bound Ru(phen)$_3^{2+}$ due to the additional adsorption of Δ-Ni(phen)$_3^{2+}$ at its neighboring sites.

Figure 6 shows the results when the enantiomers of Fe(phen)$_3^{2+}$ were added to a solution of Λ-Ru(phen)$_3^{2+}$–montmorillonite. $\Delta A(\theta = 0^\circ)$ was measured at 540 nm, where only Fe(phen)$_3^{2+}$ absorbed the monitoring light. For M* = Λ-Fe(phen)$_3^{2+}$, $\Delta A(\theta = 0^\circ)$ increased gradually until it approached a saturated value of 0.022 above $p = 3$ (curve a). The tendency was interpreted in terms of the replacement of a bound Λ-Ru(phen)$_3^{2+}$ with an added Λ-Fe(phen)$_3^{2+}$. For M* = Δ-Fe(phen)$_3^{2+}$, $\Delta A(\theta = 0^\circ)$ increased more steeply to a maximum value of 0.023 at $p = 1$ (curve b). The fact that $\Delta A(\theta = 0^\circ)$ for Δ-Fe(phen)$_3^{2+}$ leveled off more rapidly than that for Λ-Fe(phen)$_3^{2+}$ indicated that the Δ isomer did not replace the bound Ru(phen)$_3^{2+}$ but that it was adsorbed by Λ-Ru(phen)$_3^{2+}$–montmorillonite directly. Therefore, Δ-Fe(phen)$_3^{2+}$ was concluded to form a "pseudoracemic pair" with Λ-Ru(phen)$_3^{2+}$ as already derived for Ni(phen)$_3^{2+}$.

Figure 7 shows the dependences of $\Delta A(\theta = 0^\circ)$ at 450 nm due to bound Ru(phen)$_3^{2+}$ on p for other kinds of added metal complexes. Curve a shows the results for M* = Λ-Co(en)$_3^{3+}$ ($\triangle$) and Δ-Co(en)$_3^{3+}$ (○). For both cases, the plots fall on identical curves, indicating that there existed no stereospecificity in the interaction of Co(en)$_3^{3+}$ with Λ-Ru(phen)$_3^{2+}$–montmorillonite. The observation that $\Delta A(\theta = 0^\circ)$ approached zero above $p = 6$ implied that Co(en)$_3^{3+}$ replaced Ru(phen)$_3^{2+}$ completely at a large excess of Co(en)$_3^{3+}$.

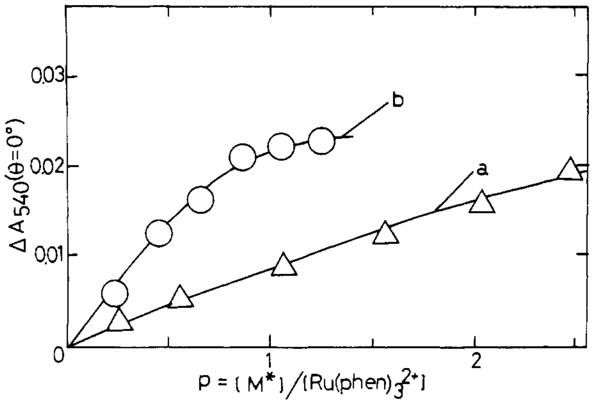

Figure 6. Plots of $\Delta A_{540}(\theta = 0^\circ)$ for a solution of Λ-Ru(phen)$_3^{2+}$–montmorillonite against the ratio of newly added Fe(phen)$_3^{2+}$ to initially present Λ-Ru(phen)$_3^{2+}$ [(Λ-Ru(phen)$_3^{2+}$–montmorillonite] = 6×10^{-6} M): curve a ($\triangle$), Λ-Fe(phen)$_3^{2+}$ added; curve b (○), Δ-Fe(phen)$_3^{2+}$ added.

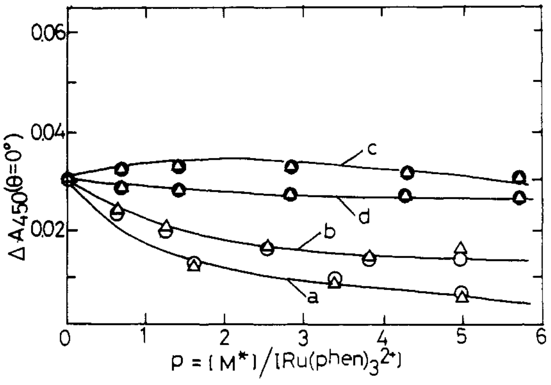

Figure 7. Plots of $\Delta A_{450}(\theta = 0^\circ)$ for a solution of Λ-Ru(phen)$_3^{2+}$–montmorillonite against the ratio of newly added complex (M*) to initially present Λ-Ru(phen)$_3^{2+}$ ([Λ-Ru(phen)$_3^{2+}$–montmorillonte] = 6×10^{-6} M). The added complexes were as follows: curve a, ($\triangle$) Λ-Co(en)$_3^{3+}$ and (○) Δ-Co(en)$_3^{3+}$; curve b, ($\triangle$) Λ-Co(phen)$_3^{3+}$ for Λ-Ru(phen)$_3^{2+}$–montmorillonite and (○) Λ-Co(phen)$_3^{3+}$ for Δ-Ru(phen)$_3^{2+}$–montmorillonite; curve c, racemic Co(phen)$_3^{2+}$; curve d, racemic Ni(phen)$_3^{2+}$.

Curve b was the result when Λ-Co(phen)$_3^{3+}$ was added to a solution of Λ-Ru(phen)$_3^{2+}$–montmorillonite ($\triangle$) or Δ-Ru(phen)$_3^{2+}$–montmorillonite (○). For both cases, $\Delta A(\theta = 0^\circ)$ decreased gradually until it leveled off at the value of 0.014 above $p = 5$. Thus it was concluded that Co(phen)$_3^{3+}$ replaced bound Ru(phen)$_3^{2+}$ with no stereospecificity. Since $\Delta A(\theta = 0^\circ)$ did not become zero at large p, some part of the initially bound Ru(phen)$_3^{2+}$ might be attracted toward Δ-Co(phen)$_3^{3+}$–montmorillonite. This again suggests the attractive interaction between Co(phen)$_3^{3+}$ and Ru(phen)$_3^{2+}$ on a clay surface.

Curves c and d exhibit the results when racemic mixtures of Co(phen)$_3^{2+}$ and Ni(phen)$_3^{2+}$ were added to a solution of Λ-Ru(phen)$_3^{2+}$–montmorillonite, respectively. For M* = racemic Co(phen)$_3^{2+}$, $\Delta A(\theta = 0^\circ)$ increased a little initially until it reached a broad maximum around $p = 2$. Contrary to this, $\Delta A(\theta = 0^\circ)$ for M* = racemic Ni(phen)$_3^{2+}$ decreased slightly in the range $p = 1$–6. The origin for the observed differences might lie in the differences in the lability for racemization between these two complexes. That is, Co(phen)$_3^{2+}$ racemizes rapidly with a half-life of less than 1 s, while Ni(phen)$_3^{2+}$ racemizes slowly with a half-life of 35 h at 25 °C.[5,12] On the basis of these facts, the Λ and Δ enantiomers of racemic Ni(phen)$_3^{2+}$ were expected to interact with a clay as different chemical species. In other words, Δ-Ni(phen)$_3^{2+}$ was adsorbed by Λ-Ru(phen)$_3^{2+}$–montmorillonite directly, while

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(12) Blinn, E. L.; Wilkins, R. G. *Inorg. Chem.* **1976**, *15*, 2952.

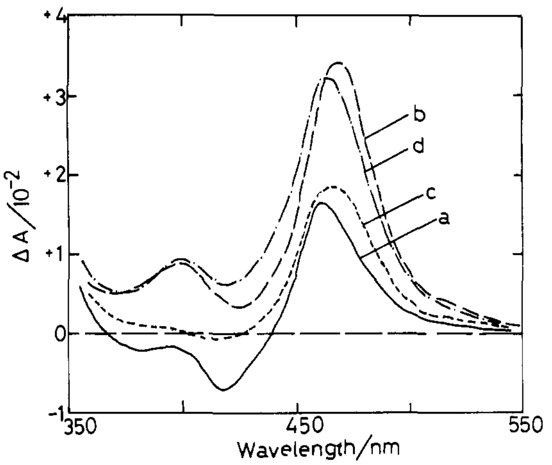

Figure 8. CD spectra of an aqueous solution of Λ-Ru(phen)$_3$(ClO$_4$)$_2$: curve a, [Λ-Ru(phen)$_3$(ClO$_4$)$_2$] = 1.5×10^{-5} M; curve b, 3.0×10^{-5} M clay added to the first solution; curve c, 2.0×10^{-5} M Λ-Ni(phen)$_3$(ClO$_4$)$_2$ added to the mixture; curve d, 2.0×10^{-5} M Δ-Ni(phen)$_3$(ClO$_4$)$_2$ added to the mixture. The cell length was 10 cm.

Λ-Ni(phen)$_3^{2+}$ replaced Λ-Ru(phen)$_3^{2+}$ on a clay. The observed tendency in $\Delta A(\theta = 0°)$ was the overlap of these two processes. Contrary to this, Co(phen)$_3^{2+}$ would be adsorbed by the clay only in the form of Δ-Co(phen)$_3^{2+}$, since this form of the chelate was adosrbed without replacing bound Λ-Ru(phen)$_3^{2+}$. The observed trend in $\Delta A(\theta = 0°)$ was consistent with this mechanisms.

(2) Circular Dichroism Studies on Adsorption of Metal Chelates by a Colloidal Clay. The adsorption of an optically active metal chelate by a colloidal clay was studied by means of circular dichroism (CD) measurements. Figure 8 shows the effects of a clay on the CD absorption of Ru(phen)$_3^{2+}$. Free Λ-Ru(phen)$_3^{2+}$ exhibited the spectral shape in the wavelength region of 350–550 nm as shown by curve a. On the addition of a clay to the solution, the two peaks with opposite signs at 420 and 465 nm displaced in the upward direction until the CD absorptions at both peaks became positive (curve b). The above two peaks in the CD spectrum arose from the long-axis charge-transfer excitations from a central metal to the ligands coupled with the ligand excitation of the same polarization.[8] Apparently the observed CD change was due to the binding of free Ru(phen)$_3^{2+}$ with a clay. On a clay the Ru(II) chelate would interact with its neighboring Ru(phen)$_3^{2+}$ and also with a clay surface. When the variation of the CD absorption at 465 nm was plotted against the ratio of a clay to Ru(phen)$_3^{2+}$, it increased linearly until it leveled off at the ratio of 2 (not shown). The results were consistent with the conclusion that Ru(phen)$_3^{2+}$ was adsorbed by a clay and occupied two cation-exchange sites per chelate when the chelate was added as a pure enantiomer.

When Λ-Ni(phen)$_3^{2+}$ was added to a solution of Λ-Ru(phen)$_3^{2+}$–montmorillonite, the spectrum changed as shown from curve b to curve c. The results were interpreted in terms of the dissociation of bound Ru(phen)$_3^{2+}$ to a free ion under the attack of Λ-Ni(phen)$_3^{2+}$. On the other hand, when Δ-Ni(phen)$_3^{2+}$ was added to the same solution, the spectrum changed little from curve b to curve d as shown. In this case, no dissociation of bound Λ-Ru(phen)$_3^{2+}$ occurred but added Δ-Ni(phen)$_3^{2+}$ was likely to be adsorbed by Λ-Ru(phen)$_3^{2+}$–montmorillonite directly. These results were completely consistent with the preceeding electric dichroism results (Figure 5).

Figure 9 shows the effects of Co(phen)$_3^{2+}$ on the CD spectrum of Λ-Ru(phen)$_3^{2+}$–montmorillonite. When racemic Co(phen)$_3^{2+}$ was added to a solution of Λ-Ru(phen)$_3^{2+}$–montmorillonite, the CD spectrum changed from curve a to curve b. The observed change was interpreted in terms of the appearance of the two peaks with opposite signs as shown by the difference spectrum between curves a and b (curve c). The results suggested that the Δ isomers of some tris(phenanthroline) chelates were produced in excess in the solution. On the basis of the electric dichroism results in the previous section, it was concluded that the racemization equilibrium in added Co(phen)$_3^{2+}$ was displaced toward excess Δ-Co(phen)$_3^{2+}$ due to binding with Λ-Ru(phen)$_3^{2+}$–montmorillonite. Such conversion of Λ-Co(phen)$_3^{2+}$ to Δ-Co(phen)$_3^{2+}$ was induced by the stabilization of the Δ form of Co(phen)$_3^{2+}$ due to the "pseudoracemic pairing" with bound Λ-Ru(phen)$_3^{2+}$ on a clay surface.

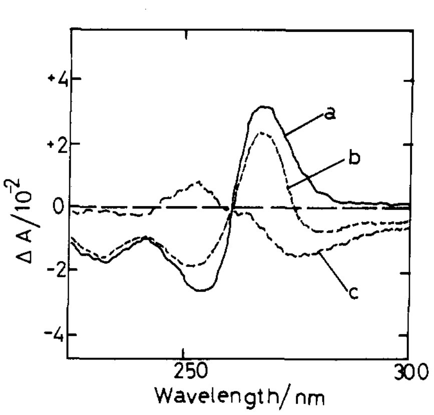

Figure 9. Effects of racemic Co(phen)$_3$(ClO$_4$)$_2$ on the CD of Λ-Ru(phen)$_3^{2+}$–montmorillonite: curve a, spectrum for [Λ-Ru(phen)$_3^{2+}$–montmorillonite] = 1.5×10^{-6} M; curve b, spectrum after 2.0×10^{-6} M racemic Co(phen)$_3$(ClO$_4$)$_2$ was added to the first solution; curve c, difference spectrum between curves a and b. The cell length was 1 cm.

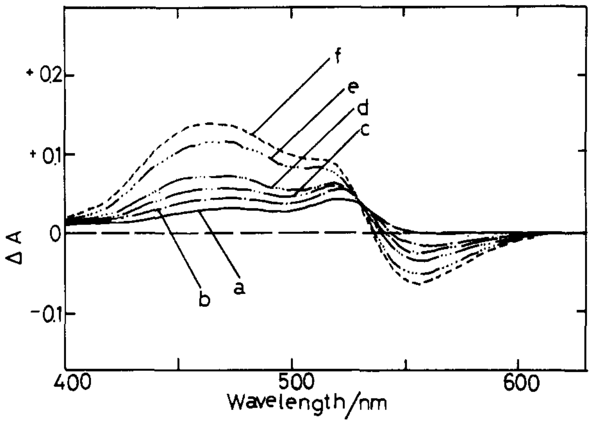

Figure 10. Induction of CD spectra of a racemic solution of Fe(phen)$_3$(ClO$_4$)$_2$ in the presence of Δ-Ni(phen)$_3^{2+}$–montmorillonite. The CD spectra were recorded at various intervals after 1.5×10^{-5} M racemic Fe(phen)$_3$(ClO$_4$)$_2$ was added to a solution of 1.5×10^{-5} M Δ-Ni(phen)$_3^{2+}$–montmorillonite: (a) 2 min after mixing; (b) 5 min after mixing; (c) 15 min after mixing; (d) 30 min after mixing; (e) 3 h after mixing. Curve f shows the spectrum when 1.5×10^{-5} M Λ-Fe(phen)$_3$(ClO$_4$)$_2$ was added to a solution of Δ-Ni(phen)$_3^{2+}$–montmorillonite. The cell length was 10 cm.

In Figure 10, racemic Fe(phen)$_3^{2+}$ was added to a solution of Δ-Ni(phen)$_3^{2+}$–montmorillonite. In the absence of Fe(phen)$_3^{2+}$, no CD absorption was observed in the visible region from 400 to 700 nm. When Fe(phen)$_3^{2+}$ was added, the CD absorption was induced instantly as shown by curve a. The absorption changed with time as shown by curves b–d until reaching the final spectrum, curve e, after about 3 h. The final spectrum was similar to curve f, which was obtained by adding Λ-Fe(phen)$_3^{2+}$ to a solution of Δ-Ni(phen)$_3^{2+}$–montmorillonite. It was concluded, therefore, that added Fe(phen)$_3^{2+}$ converted to bound Λ-Fe(phen)$_3^{2+}$ on a clay surface. The change from curve a to curve e, therefore, corresponded to the antiracemization process of racemic Fe(phen)$_3^{2+}$ to Λ-Fe(phen)$_3^{2+}$. As already concluded for Co(phen)$_3^{2+}$, the Λ form of Fe(phen)$_3^{2+}$ was stabilized due to the "pseudoracemic pairing" with Δ-Ni(phen)$_3^{2+}$ on a clay. The fact that initially present Δ-Ni(phen)$_3^{2+}$ racemized partially within 3 h might explain why Fe(phen)$_3^{2+}$ did not antiracemize to 100% (compare curve e and curve f). Instantaneous induction of CD absorption at curve a was ascribed to the difference of CD absorption between bound Λ-Fe(phen)$_3^{2+}$ and free Δ-Fe(phen)$_3^{2+}$. Only Λ-Fe(phen)$_3^{2+}$ was adsorbed by Δ-Ni(phen)$_3^{2+}$–montmorillonite at the instant

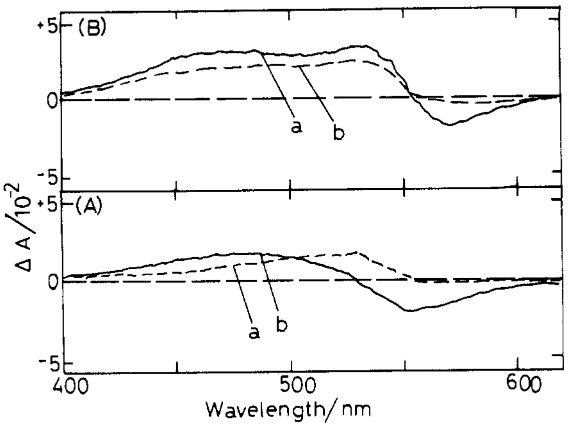

Figure 11. Induction of CD spectra of a racemic solution of (A) $Fe(bpy)_3(ClO_4)_2$ or (B) $Fe(batho)_3(ClO_4)_2$ in the presence of Δ-$Ni(phen)_3^{2+}$–montmorillonite (1.5×10^{-5} M). The concentrations of added Fe complexes were 1.5×10^{-5} M. The spectra were recorded at 2 min (curve a) and 3 h (curve b) after mixing. Cell length was 10 cm.

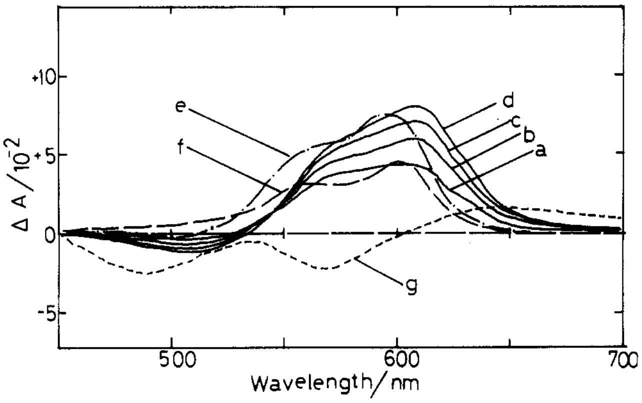

Figure 12. Induction of CD spectra of a racemic solution of $M(PAN)_2$ in the presence of Δ-$Ni(phen)_3^{2+}$–montmorillonite (1.5×10^{-5} M): curves a–d, 1.5×10^{-5} M $Cu(PAN)_2$ with spectra recorded at (a) 2 min, (b) 29 min, (c) 52 min, and (d) 75 min after mixing; curve e, 1.5×10^{-5} M $Zn(PAN)_2$; curve f, 1.5×10^{-5} M $Ni(PAN)_2$. Curve g shows the CD spectrum of 2×10^{-5} M $(-)_D$-$Co(PAN)_2$. The cell length was 10 cm.

that racemic $Fe(phen)_3^{2+}$ was added to the solution.

Similar induction of CD absorption was observed when racemic mixtures of $Fe(bpy)_3^{2+}$ and $Fe(batho)_3^{2+}$ were added to a solution of Δ-$Ni(phen)_3^{2+}$–montmorillonite (Figure 11A,B), respectively. The results indicated that both $Fe(bpy)_3^{2+}$ and $Fe(batho)_3^{2+}$ antiracemized to the Λ enantiomers due to the "pseudoracemic pairing" with bound Δ-$Ni(phen)_3^{2+}$ on a clay surface. Such antiracemization was not seen when racemic $Fe(batho\text{-}SO_3)_3^{4-}$ was added to the Δ-$Ni(phen)_3^{2+}$–montmorillonite. This was most likely because negatively charged $Fe(batho\text{-}SO_3)_3^{4-}$ was not adsorbed by a clay.

Figure 12 shows the CD spectra when $Cu(PAN)_2$ was added to a solution of Δ-$Ni(phen)_3^{2+}$–montmorillonite. The positive peaks appeared at 575 and 610 nm instantly. The absorptions changed gradually with time as shown by curves a–d. After 1 h, it reached the stationary spectrum (curve d) in which a small negative peak appeared at 515 nm. Such induction of CD spectra was not seen when $Cu(PAN)^+$ was added to a solution of Δ-$Ni(phen)_3^{2+}$–montmorillonite. When $Ni(PAN)_2$ and $Zn(PAN)_2$ were added, the instantaneous induction of CD absorption was observed, being followed by the change of the spectrum with time (curves e and f, respectively.) The above CD spectra were apparently induced by the interaction of PAN ligands in a bound chelate with Δ-$Ni(phen)_3^{2+}$ on a clay surface. The final spectra (curves d–f), however, were not attributed to the optically active $M(PAN)_2$ chelates as concluded for the cases of $Co(phen)_3^{2+}$ and $Fe(phen)_3^{2+}$. This was derived on the basis of the following observations: (i) After the final solution, which gave the spectrum shown in curve d, was filtered, a precipitate was obtained. No CD was observed when the $Cu(PAN)_2$ in such a precipitate was washed into methanol. In other words, optical activity was detected only when $Cu(PAN)_2$ was present with Δ-$Ni(phen)_3^{2+}$–montmorillonite. It was not likely that optically active $Cu(PAN)_2$ racemized during the washing procedure because the development of the CD spectra from curve a to curve d in Figure 12 took about 1 h. (ii) $Co(PAN)_2$ was previously resolved by liquid column chromatography.[13] The CD spectrum of $(-)_D$-$Co(PAN)_2$ was displayed by curve g in Figure 12, which consisted of two peaks with opposite signs in the region of 550–700 nm. Since the CD absorption in this wavelength region arose from the interaction between the two coordinated PAN ligands, the spectrum should be similar to those of optically active $Cu(PAN)_2$ and other kinds of $M(PAN)_2$ chelates. There was, however, no resemblance between the spectrum of curve g and the spectra of curves d–f. On the basis of these observations, it was concluded that no antiracemization of $M(PAN)_2$ took place on Δ-$Ni(phen)_3^{2+}$–montmorillonite, but spectra d–f were induced because of the difference of the CD absorptions between the opposite enantiomers of bound $M(PAN)_2$ molecules. It was not certain what kind of molecular processes were responsible for the observed CD changes with time.

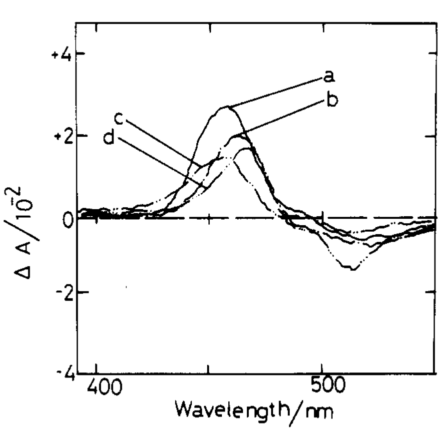

Figure 13. Induction of CD spectra of an aqueous solution of the N-alkylated acridine orange cation in the presence of Δ-$Ni(phen)_3^{2+}$–montmorillonite (1.5×10^{-5} M): curve a, acridine orange hydrochloride; curve b, *N*-methyl acridine orange iodide; curve c, *N*-ethyl acridine orange iodide; curve d, *N*-*n*-propyl acridine orange iodide. The dye concentrations were 1×10^{-5} M, and the cell length was 10 cm.

In the above results the optical activity was induced in a racemic chelate bound to optically active $M(phen)_3^{2+}$–montmorillonite. Figure 13 shows that even an organic molecule that was not optically active as a free molecule became optically active when it was bound to Δ-$Ni(phen)_3^{2+}$–montmorillonite. In Figure 13, an N-alkylated acridine orange cation ($AO\text{-}R^+$) was added to a solution of Δ-$Ni(phen)_3^{2+}$–montmorillonite. The molecules were achiral and accordingly showed no CD absorption as an isolated species. The CD absorption was induced in the wavelength region of 400–500 nm in the presence of Δ-$Ni(phen)_3^{2+}$–montmorillonite, as shown in the figure. The concerned molecules possessed an intense electronic absorption band in this wavelength region. For all four investigated molecules, the CD absorptions were composed of two peaks with opposite signs. From a comparison of the spectra with the CD spectra of the acridine orange cation (AOH^+) bound to optically active polymers,[14] it was deduced that $AO\text{–}R^+$ cations formed some aggregates in which each $AO\text{–}R^+$ molecule was in an asymmetric position with respect to its neighbors.

Discussion

Electric dichroism studies on the adsorption of metal chelates by a colloidal clay revealed that the racemic adsorption as expressed by (2) was realized between two different kinds of tris(phenanthroline)metal(II) ions. Such racemic adsorption was not achieved for the systems involving tris(phenanthroline)metal(III)

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(13) Yamagishi, A. *J. Chromatogr.* **1983**, *262*, 41.

(14) Hatano, M.; Yoneyama, M.; Sato, Y. *Biopolymers* **1973**, *12*, 895.

and tris(ethylenediamine)metal(III) ions. The results were consistent with the previously proposed model that, in the racemic adsorption of $M(phen)_3^{2+}$, the Λ and Δ enantiomers were closely located on a clay surface with their phenanthroline ligands stacked stereoselectively.[1] For a pair of $M(phen)_3^{2+}$ and $M(phen)_3^{3+}$ ions, such stereoselective pairing was not realized because the electrostatic repulsion between the chelates overcame the attractive interaction due to the dispersive force between the phenanthroline ligands. For a pair of $M(phen)_3^{2+}$ and $M(en)_3^{3+}$ ions, attractive interaction might occur to a lesser extent between the phenanthroline ligands in $M(phen)_3^{2+}$ and the ethylenediamines in $M(en)_3^{3+}$.

Circular dichroism studies demonstrated that labile metal complexes such as $Co(phen)_3^{2+}$ and $Fe(phen)_3^{2+}$ antiracemized when adsorbed by an ion-exchange adduct of a clay and optically active $M(phen)_3^{2+}$, e.g. Λ-$Ru(phen)_3^{2+}$–montmorillonite. The results indicated that the empty sites on a clay in the state shown in (1) not only accepted the opposite enantiomer of a primary adsorbed $M(phen)_3^{2+}$ but also stabilized the configuration of an adsorbate against racemization. For the case of $Fe(phen)_3^{2+}$, about 80% of initially added $Fe(phen)_3^{2+}$ converted to the Λ enantiomer, being adsorbed by Δ-$Ni(phen)_3^{2+}$–montmorillonite. The results implied that the equilibrium constant between Δ-$Fe(phen)_3^{2+}$ and Δ-$Fe(phen)_3^{2+}$, K, were displaced from 1 to 4 in the presence of the clay adduct. This was a remarkably large shift of equilibrium in comparison with that of the previously known Pffeifer effects in solution phases. Davies and Dwyer reported that Δ-$Ni(phen)_3^{2+}$ was enriched with $K = 1.14$ at 25 °C in the presence of 2% cinchonium sulfate in 0.10 N H_2SO_4.[15] The large value of K presently observed was ascribed to the participation of a macromolecule of a colloidal clay. On such a clay surface, the adsorbed molecule might be protected from racemization as though it were separated from a bulk solution as a solid crystal.

The above tendency to select and stabilize only one enantiomer of a chelate by an adduct of an optically active chelate–montmorillonite might be of potential utility for asymmetric syntheses. That is, when some achiral molecule reacted at an empty site of a clay at the state shown in (1), the molecule would change to an optically active compound under the stereoselective control due to the preadsorbed optically active chelates. This possibility was strengthened by the facts that (i) racemic $Cu(PAN)_2$ became optically active in its electronic absorption spectrum (Figure 12) under the influence of Δ-$Ni(phen)_3^{2+}$ and that (ii) an achiral molecule, the N-substituted acridine orange cation, formed an optically active aggregate when it was adsorbed by Δ-$Ni(phen)_3^{2+}$–montmorillonite. In fact, such an effect was observed when a metal ion (Co^{2+}) was added to a solution of Δ-$Ni(phen)_3^{2+}$–montmorillonite that had adsorbed PAN ligands. Optically active $Co(PAN)_2^{+}$ was produced as a product.[16] The results were regarded as an indication that the adsorbed PAN ligands were in positions asymmetric with each other just as the acridine orange cations in the present case.

Acknowledgment. Thanks are due to Prof. K. Yagi and Prof. F. Morita (Department of Chemistry, Hokkaido University) for their permission to use the JASCO J-500A spectropolarimeter.

Registry No. $Ru(phen)_3^{2+}$, 22873-66-1; Λ-$Ru(phen)_3^{2+}$, 24162-09-2; Δ-$Ru(phen)_3^{2+}$, 19368-51-5; $Ni(phen)_3^{2+}$, 17085-38-0; Λ-$Ni(phen)_3^{2+}$, 31933-96-7; Δ-$Ni(phen)_3^{2+}$, 23385-79-7; $Fe(phen)_3^{2+}$, 14708-99-7; Λ-$Fe(phen)_3^{2+}$, 47836-89-5; Δ-$Fe(phen)_3^{2+}$, 24324-38-7; $Co(phen)_3^{2+}$, 16788-34-4; Λ-$Co(phen)_3^{3+}$, 24458-65-9; Λ-$Co(en)_3^{3+}$, 27228-84-8; Δ-$Co(en)_3^{3+}$, 16569-46-3; $Fe(bpy)_3^{2+}$, 15025-74-8; $Fe(batho)_3^{2+}$, 21412-03-3; $Cu(PAN)_2$, 22393-47-1; $Zn(PAN)_2$, 43184-71-0; $Ni(PAN)_2$, 22393-46-0; $Co(PAN)_2$, 92343-26-5; montmorillonite, 1318-93-0; acridine orange conjugate monoacid, 17251-70-6; *N*-methyl acridine orange, 21629-01-6; *N*-ethyl acridine orange, 36366-89-9; *N*-propyl acridine orange, 36366-90-2.

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(15) Davies, N. R.; Dwyer, F. P. *Trans. Faraday Soc.* **1954**, *50*, 24.

(16) Yamagishi, A. *J. Chem. Soc., Chem. Commun.* **1984**, 119.

Contribution from the Laboratoire de Chimie du Solide et Inorganique Moléculaire, UA 254, Université de Rennes I,
35042 Rennes-Cédex, France, and Department of Chemistry, Cornell University, Ithaca, New York 14853

Six- and Five-Vertex Organometallic Clusters

JEAN-FRANÇOIS HALET,[†] ROALD HOFFMANN,*[‡] and JEAN-YVES SAILLARD*[†]

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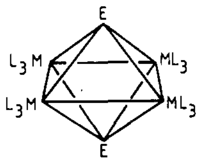
The electronic structure of closo square-bipyramidal M_4E_2 clusters (M = metal atom in an ML_3 local coordination and E = PR, GeR, S, Te, ...) is analyzed. Two electron counts are possible: there are eight or seven skeletal electron pairs whether a low-lying metal–metal π antibonding MO is occupied or not. The role of 3d orbitals of the E fragment is emphasized, and the E···E bonding interaction is analyzed. The electron count in other related closo and nido clusters is also discussed. Particularly, the possibility of six or seven electron pairs is predicted for M_4E_2 clusters where M is in an ML_2 local coordination.

The polyhedral skeletal electron pair (PSEP) theory has proved to be a powerful tool in the understanding and prediction of the structure of organometallic clusters.[1] Its simple rules have been derived on the basis of the structural and bonding pattern of polyhedral borane and carborane clusters, taking advantage of the isolobal analogy[2] of B–H and C–H fragments with d^8 and d^9 ML_3 units.

As general and fundamental as it is, the PSEP theory sometime fails,[3] as all models do. This paper deals with a family of six-vertex *closo*-M_4E_2 compounds, which often do not conform with the PSEP theory.

The structurally characterized clusters of this family are listed in Table I.[4-14] They can be well represented by the model **16**,



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where the ligand E is GeR, PR, AsR, S, or Te. In the compounds of Table I the transition metal is in an ML_3 local coordination

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[†] Université de Rennes I.

[‡] Cornell University.

(1) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1; "Transition Metal Clusters"; Johnson, F. B. G., Ed.; Wiley: New York, 1980; p 193. (b) Mingos, D. M. P. *Nature (London), Phys. Sci.* **1972**, *236*, 99. (c) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446. (d) Grimes, R. N. *Acc. Chem. Res.* **1978**, *11*, 420.

(2) For a general discussion of the isolobal analogy see: Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

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