

ADSORPTION AND SPECTROSCOPIC STUDIES ON THE INTERACTIONS OF COBALT(III) CHELATES WITH CLAYS

MASAMI KANEYOSHI,^{1,4} AKIHIKO YAMAGISHI,² MASAHIRO TANAGUCHI,² AND AKIKO ARAMATA³

¹ Department of Chemistry, College of Arts and Sciences, The University of Tokyo
Komaba, Meguro-ku, Tokyo 153, Japan

² Department of Polymer Sciences, Faculty of Sciences
Hokkaido University, Sapporo 060, Japan

³ Catalysis Research Center, Hokkaido University
Sapporo 060, Japan

Abstract—The interactions of the following three kinds of racemic and enantiomeric cobalt(III) chelates with montmorillonite and saponite are studied: $[\text{Co}(\text{en})_3]^{3+}$ (en = ethylenediamine), $[\text{Co}(\text{diNOsar})]^{3+}$ (diNOsar = (1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6,6,6]-eicosane)cobalt(III)) and $[\text{Co}(\text{diAMsar})]^{3+}$ (diAMsar = (1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6,6,6]eicosane)-cobalt(III)). At neutral pH, these complexes are adsorbed as a trivalent cation up to 90%–100% of the cation exchange capacity of a clay. No difference is observed in the maximum adsorption amount between the racemic and enantiomeric isomers. The basal spacings of the clay-chelate adducts are determined by the X-ray diffraction measurements of non-oriented powder samples: 14.3 Å for $[\text{Co}(\text{en})_3]^{3+}$ montmorillonite, 16.5 Å for $[\text{Co}(\text{diNOsar})]^{3+}$ montmorillonite, and 16.9 Å for $[\text{Co}(\text{diAMsar})]^{3+}$ montmorillonite. The results imply that the chelates form a monolayer in the interlayer space. From the one-dimensional Fourier analyses of the diffraction pattern of $[\text{Co}(\text{diNOsar})]^{3+}$ montmorillonite, the chelate is concluded to be adsorbed with its three-fold symmetry axis in parallel with the layer surface. This is in contrast with the previous results of $[\text{Ru}(\text{phen})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$, which are adsorbed with their three-fold symmetry axes perpendicular to the surface. The conclusion is consistent with the angular dependence of the infrared absorption spectrum of the film of the adduct.

Key Words—Clay-metal chelate interactions.

INTRODUCTION

A cationic metal complex is intercalated in the interlayer space of a clay. The structure and properties of a clay-metal complex adduct are attracting attention because such a system provides a unique way of assembling metal complexes on a solid surface (Fripiat, 1986; Thomas, 1988). The steric interactions of an adsorbed molecule with a clay surface and its neighboring adsorbates are expected to lead to the highly ordered molecular aggregates.

As an example of a stereoregular adsorbate layer, we have recently discovered that a racemic mixture of $[\text{Ru}(\text{phen})_3]^{2+}$ (phen = 1,10-phenanthroline) is adsorbed as a racemic pair forming a double-molecular layer (Yamagishi, 1987). Another example is that an enantiomer of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridyl) is adsorbed to form a similar double-molecular layer (Villemure, 1991; Villemure and Bard, 1990). These stereoregularities are thought to be induced by the inter-molecular interactions among the adsorbates.

In the present work, we have studied the adsorption behaviors of cobalt(III) chelates by a clay. The investigated chelates are as follows: $[\text{Co}(\text{en})_3]^{3+}$ (en

= ethylenediamine), $[\text{Co}(\text{diNOsar})]^{3+}$ (diNOsar = (1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6,6,6]-eicosane)cobalt(III)), and $[\text{Co}(\text{diAMsar})]^{3+}$ (diAMsar = (1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6,6,6]-eicosane)cobalt(III)). The structures of the chelates are shown in Figure 1. These chelates are selected because they are all tris-chelated complexes, having configurational optical isomers like $[\text{Ru}(\text{phen})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$. In contrast to $[\text{Ru}(\text{phen})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$, however, $[\text{Co}(\text{diNOsar})]^{3+}$ and $[\text{Co}(\text{diAMsar})]^{3+}$ have the nitro and amino groups in the directions of the three-fold symmetry axes, respectively. As a result, these chelates have a longer size along the three-fold symmetry axes than along the two-fold symmetry axes. Thus they may be adsorbed in a way different from $[\text{Ru}(\text{phen})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$. The latter chelates have the shortest height along the three-fold symmetry axes and are adsorbed with the three-fold symmetry axes perpendicular to a clay surface (Yamagishi, 1987). These differences are expected to cause the different stacking interactions among the adsorbed species.

Adsorption has been compared between the racemic mixtures and pure enantiomers of these chelates. In addition, the adsorption structures have been studied with spectroscopic measurements such as X-ray diffraction and infrared absorption spectra.

⁴ Present address: Laboratory of Magnetic Materials, Shin-Etsu Co. Ltd., Takefu 915, Japan.

EXPERIMENTAL METHODS

A racemic mixture of $[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ was prepared by reacting $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with ethylenediamine in water and oxidizing with air. An optical isomer having a positive sign in optical rotation at 589 nm, $(+)\text{_{589}}\text{-[Co}(\text{en})_3]\text{Cl} (+)\text{tartrate} \cdot 5\text{H}_2\text{O}$, was obtained by resolving the racemic mixture with sodium tartrate. By replacing an anion with an aqueous ZnCl_2 solution, $(+)\text{_{589}}\text{-[Co}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ was obtained: $[\text{M}]_{589}$ (molar rotation at 589 nm) = 85.4. A racemic mixture of $[\text{Co}(\text{diNOSar})]\text{Cl}_3$ was synthesized from $[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ according to the reported method (Geue *et al.*, 1984). The product was identified with the elemental analyses: C 30.88% (calc. 31.15%), H 5.86% (calc. 5.60%), N 20.98% (calc. 20.77%) and Cl 19.69% (calc. 19.70%). $(-)\text{_{589}}\text{-[Co}(\text{diNOSar})]\text{Cl}_3$ was synthesized from $(+)\text{_{589}}\text{-[Co}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ in the same way: $[\text{M}]_{589} = -265.9$. A racemic mixture of $[\text{Co}(\text{diAMSar})]\text{Cl}_3 \cdot 2\text{HCl} \cdot 1.5\text{H}_2\text{O}$ was prepared by reducing $[\text{Co}(\text{diNOSar})]\text{Cl}_3$ with Zn: C 28.91% (calc. 29.00%), H 6.64% (calc. 6.78%), N 19.28% (calc. 19.32%) and Cl 30.70% (calc. 30.58%). $(-)\text{_{589}}\text{-[Co}(\text{diAMSar})]\text{Cl}_3 \cdot 2\text{HCl}$ was obtained from $(-)\text{_{589}}\text{-[Co}(\text{diNOSar})]\text{Cl}_3$ in the same way: $[\text{M}]_{589} = -266.5$. Comparing these molecular rotations with the reported values of the similar compounds (Geue *et al.*, 1984), the optical purities of these enantiomers were estimated to be higher than 90%.

As clay samples, sodium montmorillonite (Kunipia G, Kunimine Ind. Co., Japan) and synthetic saponite (Smecton, Kunimine Ind. Co., Japan) were used. The cation-exchange capacity (CEC) and the average particle size were previously determined as follows: 114 meq/100g and 0.37 μm (sodium montmorillonite) and 80 meq/100g and 0.19 μm (saponite) (Nakamura *et al.*, 1988). A silicon wafer used for infrared absorption measurements was donated from Shin-etsu Co. Ltd (Japan).

The electronic spectra were recorded on a spectrophotometer, UVIDEK 430A (JEOL, Japan). In order to determine the adsorption amount of a metal chelate by a clay, we prepared a 25 ml aqueous suspension that contained about 1×10^{-4} mole of a metal complex and 0.0877 g of montmorillonite or 0.125 g of saponite. The pH of a suspension was adjusted at about 7 with 0.1 M $\text{KH}_2\text{PO}_4/\text{NaOH}$ buffer. After centrifuging the suspension, the concentration of an unbound chelate in a supernatant solution was determined from the electronic absorption spectrum. The adsorption experiments were repeated three times for each metal chelate. When the adsorption of a racemic mixture of a chelate was studied, the optical rotation of a supernatant solution was measured to see if there existed any stereoselectivity in binding with a clay.

The X-ray diffraction patterns on a powder sample were obtained using a diffractometer, J-20 (Rigaku, Japan). The wavelength of X-ray was 1.542 \AA ($K\alpha$ of

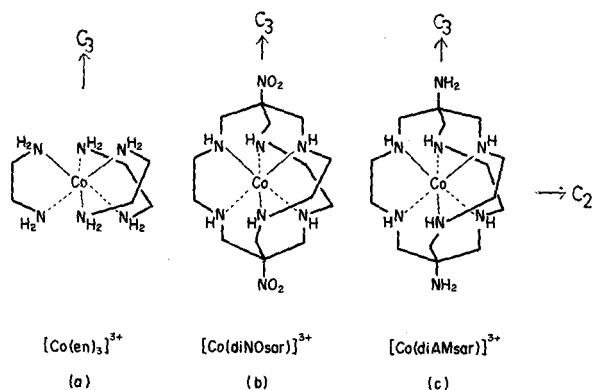


Figure 1. Structures of the investigated chelates: (a) $[\text{Co}(\text{en})_3]^{3+}$, (b) $[\text{Co}(\text{diNOSar})]^{3+}$, and (c) $[\text{Co}(\text{diAMSar})]^{3+}$.

Cu). The samples were prepared by freeze-drying the precipitates obtained after centrifuging a mixture of a clay and a chelate. No dissociation of a ligand to a supernatant solution took place during the adsorption procedures. No buffer was added in preparing the samples because a buffer was found to give no effect on adsorption of the chelates in the adsorption experiments.

The infrared spectra were measured with an infrared spectrophotometer, FT 300 (Horiba, Japan). A spectrum was measured on a film of a clay-chelate adduct. As a sample, a drop of a clay suspension was cast on a wafer of silicon single crystal and dried in air. The wafer was soaked in an aqueous solution of a chelate for several hours. The spectrum was recorded by changing the angle between the wafer surface and the incident light.

RESULTS

Table 1 shows the adsorbed amount of a chelate by montmorillonite (0.0877 g) at pH 7.2. Assuming that a chelate is adsorbed as a trivalent cation, the degree of adsorption is calculated against the CEC of a clay. As a result, these chelates are all adsorbed to almost 100% of CEC. Table 2 shows the similar results for saponite (0.125 g) at pH 7.0. The chelates are adsorbed to 90%–100% of CEC. There are 3%–6% differences in adsorption amounts between the racemic and enantiomeric chelates; however, the differences are so small that they are within the errors in the measurements. Thus, we conclude that the present chelates are adsorbed equally as racemic mixtures and enantiomers. The optical activity of a supernatant solution is measured when the racemic mixture of a chelate is adsorbed. No optical activity is detected at 589 nm (<0.01 deg dm^{-1}). The molar concentration of a chelate in a supernatant solution is estimated to be larger than 4×10^{-4} M. Taking the absolute value of the specific rotation of a chelate to be about 100° at 589 nm, the

Table 1. The adsorbed amounts of cobalt(III) chelates by montmorillonite (0.0887 g) at pH 7.2.

| Chelate | Adsorbed amount (mole) | Adsorbed amount (mol/CEC) |
|---|------------------------------|---------------------------|
| racemic $[\text{Co}(\text{en})_3]^{3+}$ | $(3.3 + 0.1) \times 10^{-5}$ | 0.33 + 0.01 |
| $(+)_589\text{-}[\text{Co}(\text{en})_3]^{3+}$ | $(3.1 + 0.2) \times 10^{-5}$ | 0.31 + 0.02 |
| racemic $[\text{Co}(\text{diNOsar})_3]^{3+}$ | $(3.0 + 0.1) \times 10^{-5}$ | 0.30 + 0.01 |
| $(+)_589\text{-}[\text{Co}(\text{diNOsar})_3]^{3+}$ | $(3.2 + 0.2) \times 10^{-5}$ | 0.32 + 0.02 |
| racemic $[\text{Co}(\text{diAMsar})_3]^{3+}$ | $(3.5 + 0.2) \times 10^{-5}$ | 0.35 + 0.02 |
| $(+)_589\text{-}[\text{Co}(\text{diAMsar})_3]^{3+}$ | $(3.4 + 0.2) \times 10^{-5}$ | 0.34 + 0.02 |

Table 2. The adsorbed amounts of cobalt(III) chelates by saponite (0.125 g) at pH 7.0.

| Chelate | Adsorbed amount (mole) | Adsorbed amount (mol/CEC) |
|---|------------------------------|---------------------------|
| racemic $[\text{Co}(\text{en})_3]^{3+}$ | $(3.3 + 0.1) \times 10^{-5}$ | 0.33 + 0.01 |
| $(+)_589\text{-}[\text{Co}(\text{en})_3]^{3+}$ | $(3.5 + 0.2) \times 10^{-5}$ | 0.35 + 0.02 |
| racemic $[\text{Co}(\text{diNOsar})_3]^{3+}$ | $(3.0 + 0.1) \times 10^{-5}$ | 0.30 + 0.01 |
| $(+)_589\text{-}[\text{Co}(\text{diNOsar})_3]^{3+}$ | $(3.2 + 0.2) \times 10^{-5}$ | 0.32 + 0.02 |
| racemic $[\text{Co}(\text{diAMsar})_3]^{3+}$ | $(3.0 + 0.1) \times 10^{-5}$ | 0.30 + 0.02 |
| $(+)_589\text{-}[\text{Co}(\text{diAMsar})_3]^{3+}$ | $(3.0 + 0.2) \times 10^{-5}$ | 0.30 + 0.02 |

enantiomer excess of a supernatant solution is calculated to be less than 0.3%. Based on this, the optical isomers of the chelates are concluded to be adsorbed with no stereoselectivity.

Figure 2 shows an example of the diffraction patterns for an adduct of montmorillonite and $[\text{Co}(\text{diNOsar})_3]^{3+}$. From the (001) diffractions, the basal spacings of the adducts are obtained as tabulated in Table 3. The last column of the table gives the height of the interlayer space, h , which is estimated by subtracting the thickness of the layer (9.5 Å for both montmorillonite and saponite) from the basal spacing (Bailey, 1984). There is no difference in the basal spacing between racemic and enantiomeric $[\text{Co}(\text{diNOsar})_3]^{3+}$ chelates.

Using the intensities of (00 l) diffractions for an adduct of $(-)_589\text{-}[\text{Co}(\text{diNOsar})_3]^{3+}$ montmorillonite, one-dimensional Fourier analyses were carried out to obtain the electron density profile along the perpendicular direction to a clay layer. For the analyses, eight diffractions from (001) to (009) except for (004) were used. The intensity of (004) was difficult to estimate correctly because the peak overlapped with the peak due to (hkl) ($h^2 + k^2 \neq 0$). The intensity of each peak is given in

Table 4 together with the observed structure factor, F_{obs} . The theoretical structure factor, F_{calc} , was also calculated when the chelate was located in the middle of the interlayer space under a various orientation. The most probable orientation was sought by comparing the observed and calculated structure factors. As a result, the difference between them, $R = F_{\text{calc}} - F_{\text{obs}}$, called the R factor, took the minimum value when the chelate took an orientation as shown in Figure 3. $[\text{Co}(\text{diNOsar})_3]^{3+}$ was adsorbed with the three-fold symmetry axis in parallel with the silicate sheet. The two-fold symmetry axis oriented perpendicularly to the surface. Under this orientation, the R factor was found to be 33.7%.

Figure 4 shows the infrared spectrum of a montmorillonite film. Here an incident angle, θ , was defined as an angle between the monitoring light and a wafer surface. With the increase of θ , the absorption peak at 650 cm^{-1} increased in intensity. The peak was assigned to the stretching mode of Si-O in Si-O-Al (or -Mg) (Sutabican and Roy, 1961). The dependence of the peak intensity on θ confirms that the clay layers in the film were oriented with the axial Si-O-Al bonds per-

Table 3. Basal spacings of clay-chelate adducts.

| Chelate | Clay | Basal spacing | Height of interlayer space, h (Å) |
|---|-----------------|---------------|-------------------------------------|
| none | montmorillonite | 12.6 | 3.1 |
| none | saponite | 12.5 | 3.0 |
| $(-)_589\text{-}[\text{Co}(\text{en})_3]^{3+}$ | saponite | 14.3 | 4.8 |
| $(-)_589\text{-}[\text{Co}(\text{en})_3]^{3+}$ | montmorillonite | 14.3 | 4.8 |
| $(-)_589\text{-}[\text{Co}(\text{diNOsar})_3]^{3+}$ | saponite | 16.1 | 6.6 |
| $(-)_589\text{-}[\text{Co}(\text{diNOsar})_3]^{3+}$ | montmorillonite | 16.5 | 7.0 |
| racemic $[\text{Co}(\text{diNOsar})_3]^{3+}$ | saponite | 16.4 | 6.9 |
| $(-)_589\text{-}[\text{Co}(\text{diAMsar})_3]^{3+}$ | saponite | 16.0 | 6.5 |
| $(-)_589\text{-}[\text{Co}(\text{diAMsar})_3]^{3+}$ | montmorillonite | 16.9 | 7.4 |

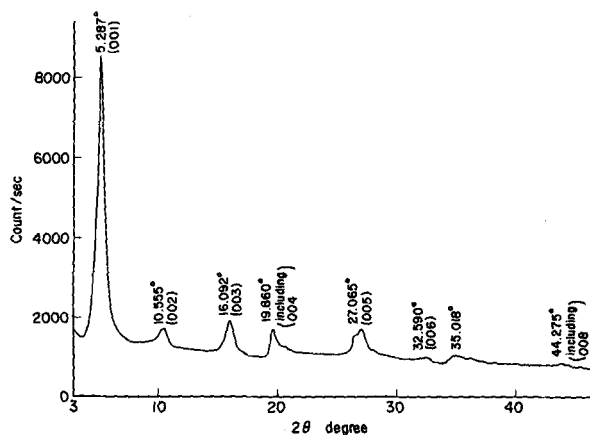


Figure 2. X-Ray diffraction pattern of a powder sample of $(-)_589\text{-[Co(diNOsar)]}^{3+}$ montmorillonite. The X-ray wavelength is 1.542 Å (Cu $K\alpha$ line).

pendicular to the surface of a silicon wafer. The same results were obtained for a saponite film.

Figure 5 is the infrared spectrum of a film of racemic $[\text{Co(diNOsar)}]^{3+}$ montmorillonite. The peaks at 1560 cm^{-1} and 1350 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the nitro groups in the chelate (Silverstein *et al.*, 1974). The peak at 1350 cm^{-1} increased by about 30% in intensity for the

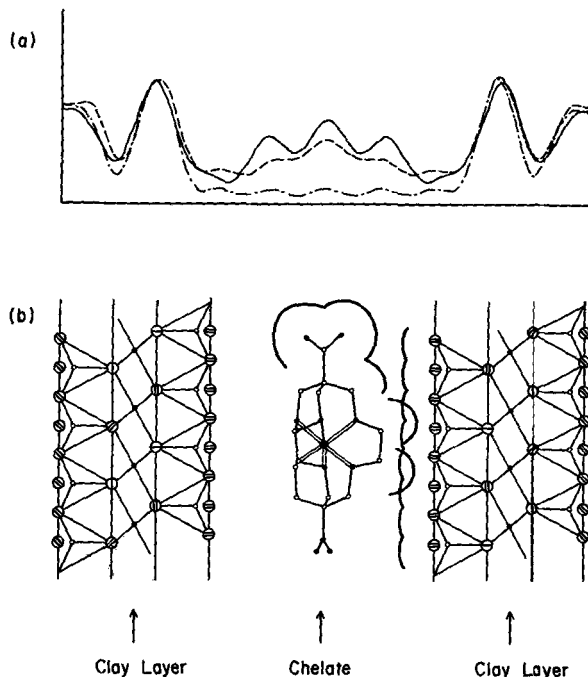


Figure 3. Electron density curve along the direction normal to the basal plane for $(-)_589\text{-[Co(diNOsar)]}^{3+}$ montmorillonite. The curves (—), (---) and (-.-) denote the observed and calculated densities of $[\text{Co(diNOsar)}]^{3+}$ montmorillonite and the observed density of montmorillonite alone, respectively.

Table 4. The observed and calculated structure factors for an adduct of $(-)_589\text{-[Co(diNOsar)}_3]^{3+}$ montmorillonite.

| (001) | F_{obs} | F_{calc} | Residue |
|-------|------------------|-------------------|---------|
| 1 | 150.6 | 250.7 | 100.0 |
| 2 | 97.9 | 68.7 | 29.1 |
| 3 | 180.4 | -159.2 | 21.2 |
| 4 | 0.0 | 59.1 | 59.1 |
| 5 | 204.0 | 172.9 | 31.0 |
| 6 | 154.5 | 152.8 | 1.6 |
| 7 | 0.0 | -13.6 | 13.6 |
| 8 | 0.0 | -89.3 | 89.3 |
| 9 | 110.1 | -93.8 | 16.2 |
| Sum | 898.4 | | 302.5 |

R factor = 33.9%.

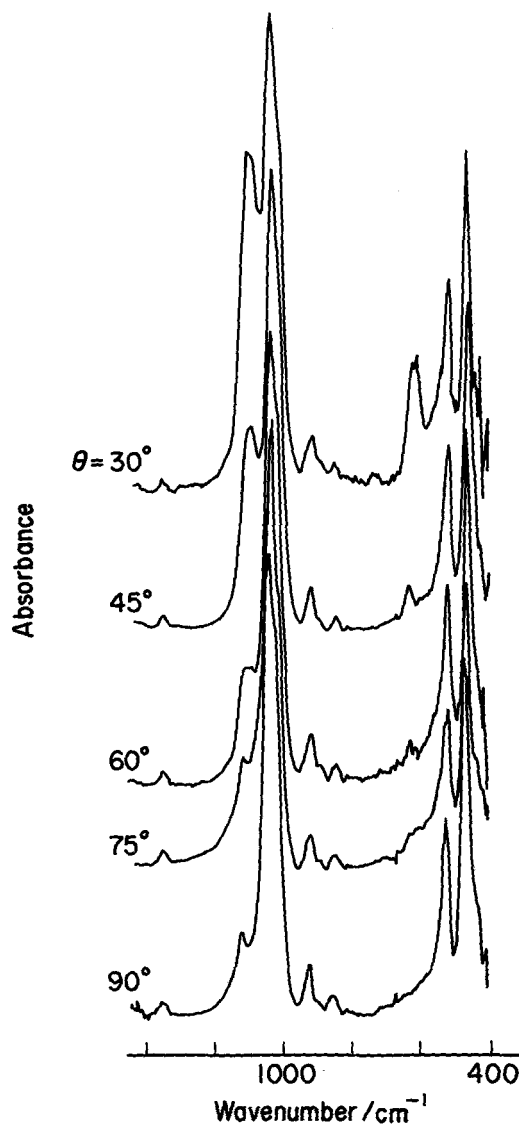


Figure 4. Infrared absorption spectra of a montmorillonite film in the range of 400–1400 cm^{-1} . θ denotes the angle between the incident light and the film surface.

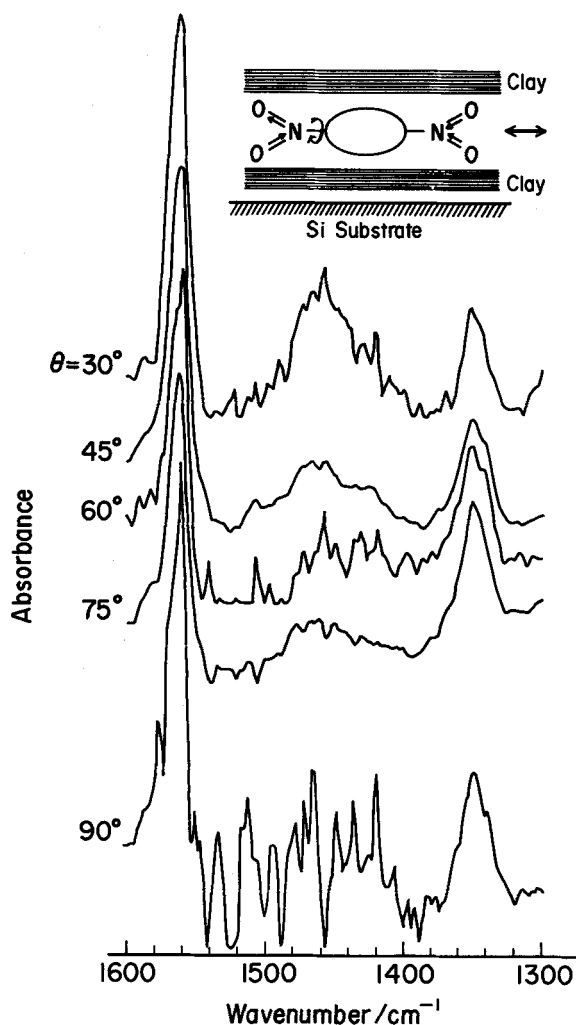


Figure 5. Infrared absorption spectra of a racemic $[\text{Co}(\text{diNOSar})]^{3+}$ montmorillonite film in the range of 1300–1600 cm^{-1} . θ denotes the angle between the incident light and the film surface. The inset exhibits the possible orientation of the nitro groups in the bound chelate.

increase of θ from 30° to 90° . The peak at 1560 cm^{-1} stayed constant for this change of θ . The interpretation of the results will be given in the following section.

DISCUSSION

From the results in Tables 1 and 2, the investigated cobalt(III) chelates are adsorbed at neutral pH almost up to 100% of CEC if these molecules are assumed to be trivalent ions. The deprotonation of $[\text{Co}(\text{diNOSar})]^{3+}$ is reported to take place above $\text{pH} = 8$ ($\text{pK}_a = 8.85$, 25°C) and the protonation of $[\text{Co}(\text{diAMSar})]^{3+}$ below $\text{pH} = 3$ ($\text{pK}_a = 3.1$ at 25°C) (Geue *et al.*, 1984); therefore, all of the investigated chelates are present as a trivalent cation in water medium at neutral pH.

According to the elemental compositions of the present clay samples, the charge of $-3 e$ in a clay layer

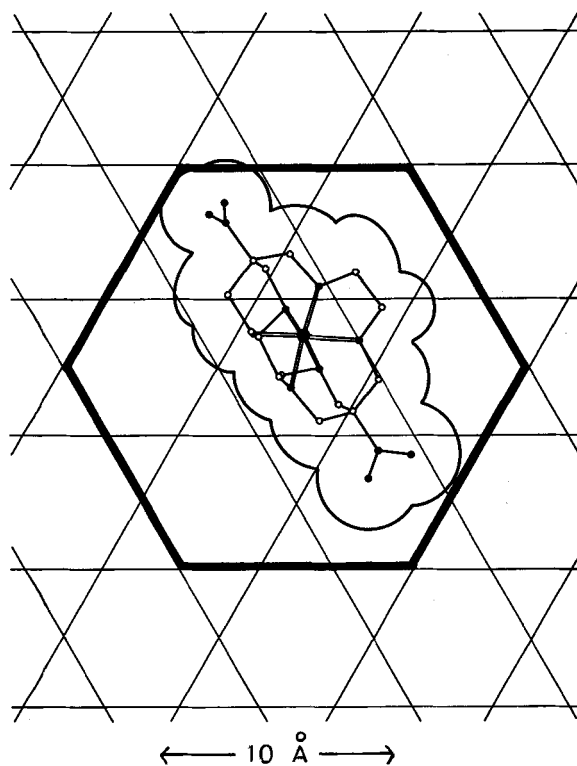


Figure 6. The possible binding state of $[\text{Co}(\text{diNOSar})]^{3+}$ by a silicate sheet of a clay. The chelate orientates the three-fold symmetry axis in parallel with the surface. The encircled hexagon denotes an area occupied by one adsorbate for the case of montmorillonite.

covers the surface area as encircled in Figure 6 for montmorillonite. Thus, the results imply that the negative charge deficiency in this area is neutralized by an adsorbed chelate at 100% CEC adsorption. No significant difference was observed in adsorption amount between a racemic mixture and a pure enantiomer. This implies that the adsorbed chelates do not interact stereoselectively on a clay surface.

The height of an interlayer space of a clay-chelate adduct, h , is obtained from the X-ray diffraction analyses (see Table 3). For $(-)_589\text{-}[\text{Co}(\text{en})_3]^{3+}$ -montmorillonite and $(-)_589\text{-}[\text{Co}(\text{en})_3]^{3+}$ -saponite, h was determined to be 4.8 \AA . This is nearly equal to the height of the intercalated chelate when it is adsorbed with its three-fold symmetry axis perpendicular to the surface. For $(-)_589\text{-}[\text{Co}(\text{diNOSar})]^{3+}$ -montmorillonite and $(-)_589\text{-}[\text{Co}(\text{diNOSar})]^{3+}$ -saponite, h was calculated to be 7.0 \AA and 6.6 \AA , respectively. These values are smaller than the length of the chelate along the three-fold symmetry axis (8 \AA); thus, it is suspected that the chelate is adsorbed with its three-fold symmetry axis in parallel with or tilted from the clay surface. For $(-)_589\text{-}[\text{Co}(\text{diAMSar})]^{3+}$ -montmorillonite and $(-)_589\text{-}[\text{Co}(\text{diAMSar})]^{3+}$ -saponite, h was 7.4 \AA and 6.5 \AA , respectively. The results indicate that $[\text{Co}(\text{diAMSar})]^{3+}$

is also adsorbed with its three-fold symmetry axis in parallel with the clay surface. According to the one-dimensional Fourier analyses of an adduct of montmorillonite and $[\text{Co}(\text{diNOsar})]^{3+}$, it is suggested that the chelate is intercalated with the three-fold symmetry axis in parallel with the clay surface as shown in Figure 3.

The binding structure in Figure 3 was compared with the results of the infrared absorption spectra (Figure 5). Under this orientation, the transition moment of the symmetric vibration of the nitro group in $[\text{Co}(\text{diNOsar})]^{3+}$ is parallel with the clay surface (see the top figure in Figure 5). For the nonpolarized light, the dependence of the absorption intensity, I , of the symmetric vibration on the incident angle, θ , is expected as below:

$$I = (1/2)I_0 \sin^2 \theta.$$

Thus, the peak intensity of the symmetric vibration may increase with the increase of θ . The transition moment of the asymmetric vibration orients in every direction with respect to the clay surface if the nitro group rotates freely around the N-C bond. Under this orientation, the absorption intensity is expected to be independent of θ as

$$I = (1/4)I_0.$$

Thus, the peak intensity of the asymmetric vibration may stay constant with the change of θ . These expectations are well coincident with the observed dependences of both the symmetric and asymmetric absorptions on θ as shown in Figure 5.

Figure 6 shows the top view of the chelate adsorbed on a silicate sheet. The hexagon encircled by a solid line denotes the area carrying the charge of $-3e$ for the case of montmorillonite. From the figure, it is concluded that the adsorbates have little contact with one another, even at the maximum adsorption, so that no steric constraint is operative between the chelates at the neighboring adsorption sites. The situations are in contrast with the adsorptions of $[\text{Ru}(\text{phen})_3]^{2+}$ and

$[\text{Ru}(\text{bpy})_3]^{2+}$. The chelates are packed so closely that the adjacent molecules interact stereoselectively with each other.

As a conclusion, the chelates, $[\text{Co}(\text{diNOsar})]^{3+}$ and $[\text{Co}(\text{diAMSar})]^{3+}$, are adsorbed between the clay layers with their three-fold symmetry axes in parallel with the clay surface but no regularity in the distribution of optical isomers is observed on the plane of the clay surface.

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