

X-RAY DIFFRACTION PATTERNS OF MONTMORILLONITE ORIENTED FILMS EXCHANGED WITH ENANTIOMERIC AND RACEMIC TRIS(2,2'-BIPYRIDYL)RUTHENIUM(II)

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Abstract—X-ray diffraction patterns of oriented films of montmorillonite containing enantiomeric tris(2,2'-bipyridyl) ruthenium(II) chloride ($\text{Ru}(\text{bpy})_3^{2+}$) show a peak corresponding to basal spacings of approximately 27 Å. This peak is absent from the X-ray patterns of montmorillonite films containing racemic cations. A basal spacing of 27 Å is consistent with the adsorption of 2 layers of the enantiomeric cations in each interlayer space. Under the same condition only one layer of the racemic cation was intercalated (basal spacings of 17.9 Å). These results are in accord with previous reports that montmorillonite can adsorb more of the optical isomers than of the racemic mixture of $\text{Ru}(\text{bpy})_3^{2+}$. Addition of NaCl to the mixtures resulted in an increase in the level of adsorption of the racemic cations and in the appearance of a peak at 27 Å in the X-ray pattern.

Key Words—Double layer, Enantiomorphs, Intercalation, Monolayer, Montmorillonite, Surface area, Tris(2,2'-bipyridyl)ruthenium(II), X-rays.

INTRODUCTION

There is as yet no satisfactory explanation for the ability of smectite clays to distinguish between the enantiomers and the racemic mixture of tris(2,2'-bipyridyl)ruthenium(II) cations ($\text{Ru}(\text{bpy})_3^{2+}$) (Yamagishi, 1987). Because smectites are not optically active (Cairns-Smith, 1982), the source of the difference in sorption has been attributed to a packing phenomenon. Yamagishi (1987) proposed that the adsorption of $\text{Ru}(\text{bpy})_3^{2+}$ by clay minerals occurred in racemic pairs, which he assumed packed more efficiently than enantiomeric pairs, making it possible to intercalate more of the racemic mixture than of the enantiomers in the space available between the clay layers.

Aside from the fact that a more compact adsorption of the racemic cations has never been experimentally demonstrated, there are several problems with this hypothesis. First, it does not account for the differences seen at low loading levels. At small cation/clay ratios, differences are seen in the absorption and emission spectra of adsorbed $\text{Ru}(\text{bpy})_3^{2+}$. When the cation is highly diluted in the clay, packing efficiency should not matter. Yet, these differences increase with decrease of the cation/clay ratio (Joshi and Ghosh, 1989). Second, the maximum amounts of racemic and enantiomeric cations adsorbed by smectites can differ by as much as a factor of 2.6 (Villemure, 1990). How can small differences in packing efficiency have such major effects on the adsorption isotherms? Furthermore, unlike what was reported for $\text{Ru}(\text{phen})_3^{2+}$ (Yamagishi, 1985), it is the enantiomers of $\text{Ru}(\text{bpy})_3^{2+}$ that were adsorbed in larger amounts (Villemure, 1990).

In an attempt to reconcile these observations with Yamagishi's racemic-pairs adsorption hypothesis, Vil-

lemure and Bard (1990) proposed that adsorption of racemic $\text{Ru}(\text{bpy})_3^{2+}$ caused more extensive face-to-face aggregation of the clay layers than adsorption of enantiomeric $\text{Ru}(\text{bpy})_3^{2+}$. A difference in the clay morphology is consistent with the interpretation of the spectral differences in terms of more extensive intercalation of racemic than enantiomeric $\text{Ru}(\text{bpy})_3^{2+}$ (Thomas, 1988). More extensive intercalation of the racemic cations would also explain why each adsorbed racemic $\text{Ru}(\text{bpy})_3^{2+}$ covers an average of 217 Å² of the clay surface, compared to only 122 Å² for each adsorbed enantiomeric $\text{Ru}(\text{bpy})_3^{2+}$ (Villemure, 1990). An intercalated cation is in contact with two clay layers, and is expected to cover approximately twice the area of an externally adsorbed cation.

Differences in the clay aggregation should have an effect on its X-ray diffraction pattern. The present study was undertaken to test this hypothesis.

EXPERIMENTAL

The clay used was a sample of montmorillonite (SWy-1), obtained from the Source Clay Minerals Repository of The Clay Minerals Society (University of Missouri, Columbia, MO). Its sodium form was prepared and its <2.0-μm (esd) fraction separated by literature procedures (Jackson *et al.*, 1949). Its cation exchange capacity (CEC) was 0.89 meq/g (Jaynes and Bigham, 1986). $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (Aldrich) was used without further purification. Its enantiomers were separated as iodides, by treatment with potassium antimonyl tartrate (Aldrich), according to the procedure of Dwyer and Gyrfas (1949). Measured values of $[\Phi]_D$ were +6600° for the Δ-isomer and -6500° for the Λ-isomer. Comparison with literature values, +7194° and -7184° re-

spectively (Dwyer and Gyrfas, 1949), gives optical purities of 96% for the Λ -isomer and 95% for the Δ -isomer. The iodides were converted to the chlorides by stirring with AgCl.

To measure the adsorption isotherms, volumes of a clay suspension (10.0 g/liter) were mixed with volumes of stock solutions (1.0 mM) of Λ , Δ , or racemic Ru(bpy)₃²⁺. The initial cation concentration in the mixtures was increased from 0.6 mM to 0.95 mM, while the clay concentration was decreased from 4.0 g/liter to 0.50 g/liter, so that the cation/clay ratio in the mixtures varied between approximately 30 and 500% of the clay's CEC. To ensure that each mixture contained at least 5 mg of the clay, the total volume of the mixtures was gradually increased to compensate for the decrease in the clay concentration.

In all cases, flocculation of the clay occurred soon after the addition of the cation. It was especially rapid for the first few mixtures, where the clay concentrations were large. The flocs were larger in the mixtures containing the racemic cation, while they were smaller and more numerous in the mixtures containing the enantiomers. After standing for 2 days, with only occasional stirring, the mixtures were centrifuged, and the decrease in concentration of Ru(bpy)₃²⁺ in the supernatant determined by UV-visible spectroscopy (MLCT band, $\epsilon = 14,600 \text{ M}^{-1} \text{ cm}^{-1}$ at 452 nm (Kalyanasundaram, 1982)).

The oriented films (2.0 × 2.7 cm) were prepared by placing the clay sediments in small volumes of the supernatant solutions (<0.5 ml) on microscope slides, and allowing the water to evaporate overnight. The minimum thickness of the films, estimated from the amount of clay contained in each mixture (>5 mg), was of the order of 3–4 μm . Note that, although several of the films were extensively cracked, they still gave good X-ray patterns. The X-ray diffraction patterns were recorded by Mr. J. Vahtra in the Department of Geology, using a vertical goniometer, CuK α radiation and a graphite monochromator. The clay films were step scanned (step size was 0.02°2 θ ; integration time 1 second) from 2 $\theta = 2$ –30°. Measurements on a blank microscope slide with no clay film show some scattering from the glass for 2 θ angles larger than about 20°, that may be responsible for the baseline drift (see Figures 2–6). No scattering was found for 2 θ angles less than 15°, in the region of primary interest in the present study.

RESULTS

The adsorption isotherms of racemic and enantiomeric Ru(bpy)₃Cl₂ by suspensions of Na⁺-montmorillonite (<2.0- μm (esd) SWy-1) are shown in Figure 1. As expected, more of the enantiomeric than of the racemic cation was adsorbed, although the difference was smaller than previously reported (Villemure, 1990). This is attributed to the lower optical purities of the

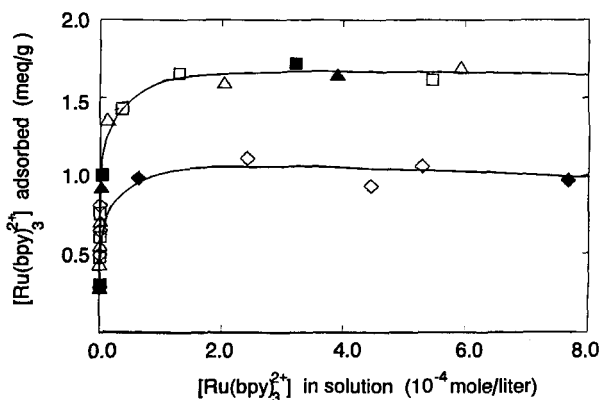


Figure 1. Adsorption isotherms of racemic and enantiomeric Ru(bpy)₃²⁺ by suspensions of the <2.0- μm (esd) fraction of Na⁺-montmorillonite, SWy-1. Diamonds, racemic mixture; triangle, Δ -enantiomer; squares, Λ -enantiomer; the filled symbols are the points that correspond to the X-ray diffraction patterns shown in Figures 2, 3 and 4.

enantiomers used in the present study. Adsorption isotherms measured after the optical purities of the enantiomers were increased to 99% by further recrystallization of the cations were similar to those in our previous report.

Figure 2 shows the X-ray diffraction patterns of oriented clay films that contained 0.28, 0.28, and 0.30 meq/g of adsorbed racemic, Δ - and Λ -Ru(bpy)₃²⁺, respectively; about 1/3 of the clay CEC. For both enantiomers, a very broad peak is seen at a 2 θ angle corresponding to a basal spacing of approximately 16 Å. This peak is much sharper for the film containing the racemic cation.

Figure 3 shows the X-ray diffraction patterns corresponding to the 5th points of the adsorption isotherms of Figure 1. These films contain 0.98, 0.92, and 1.00 meq/g of racemic, Δ - and Λ -Ru(bpy)₃²⁺, respectively; amounts just above the clay CEC. The three patterns are essentially identical. Ill-defined fourth-order, and even fifth-order, reflections can be seen. They give a 001 d-value of 17.9 Å, in complete agreement with previous reports for clays saturated with racemic Ru(bpy)₃²⁺ (Traynor *et al.*, 1978; Villemure *et al.*, 1985).

Figure 1 shows that there was no further increase in the level of adsorption of the racemic cation. Not surprisingly, no further changes are noted in the X-ray diffraction patterns of the films containing the racemic cation. For example the pattern shown in Figure 4A is practically identical to that shown in Figure 3A. This was not the case for the enantiomers. The X-ray patterns of films containing 1.65 and 1.72 meq/g of Δ - and Λ -Ru(bpy)₃²⁺, respectively (8th points of the adsorption isotherms) shown in Figures 4B,C are very different from those of Figures 3B,C. The peak around 18 Å is replaced by two ill-resolved broad peaks at approximately 27 and 17 Å. The second-order reflec-

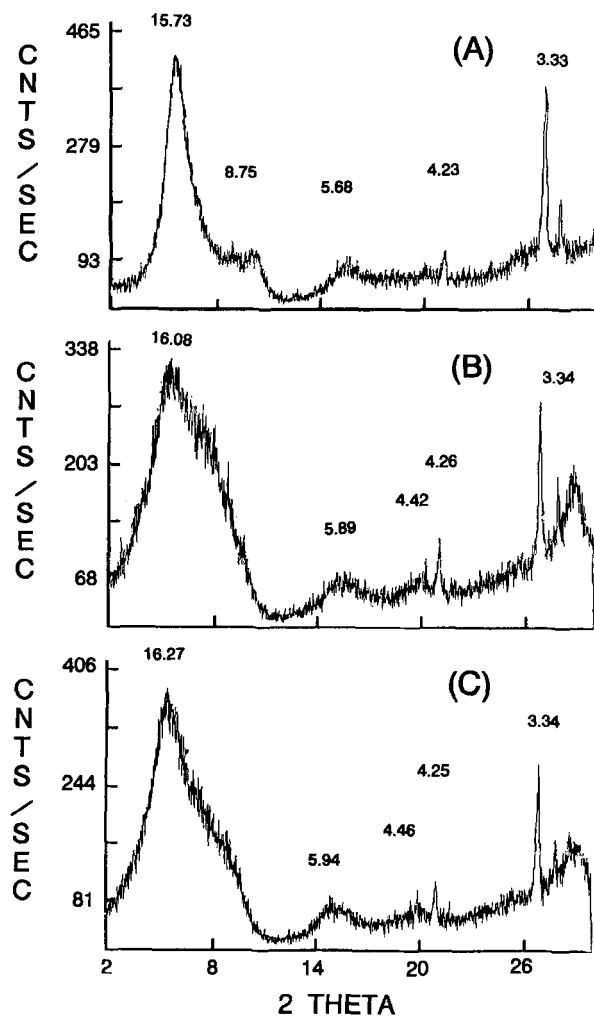


Figure 2. X-ray diffraction patterns of montmorillonite oriented films containing: A) 0.28 meq/g of adsorbed racemic $\text{Ru}(\text{bpy})_3^{2+}$, B) 0.28 meq/g of adsorbed $\Delta\text{-Ru}(\text{bpy})_3^{2+}$, C) 0.30 meq/g of adsorbed $\Delta\text{-Ru}(\text{bpy})_3^{2+}$ (1st points of the adsorption isotherms of Figure 1). The sharp peaks around 3.3 and 4.2 Å are from quartz.

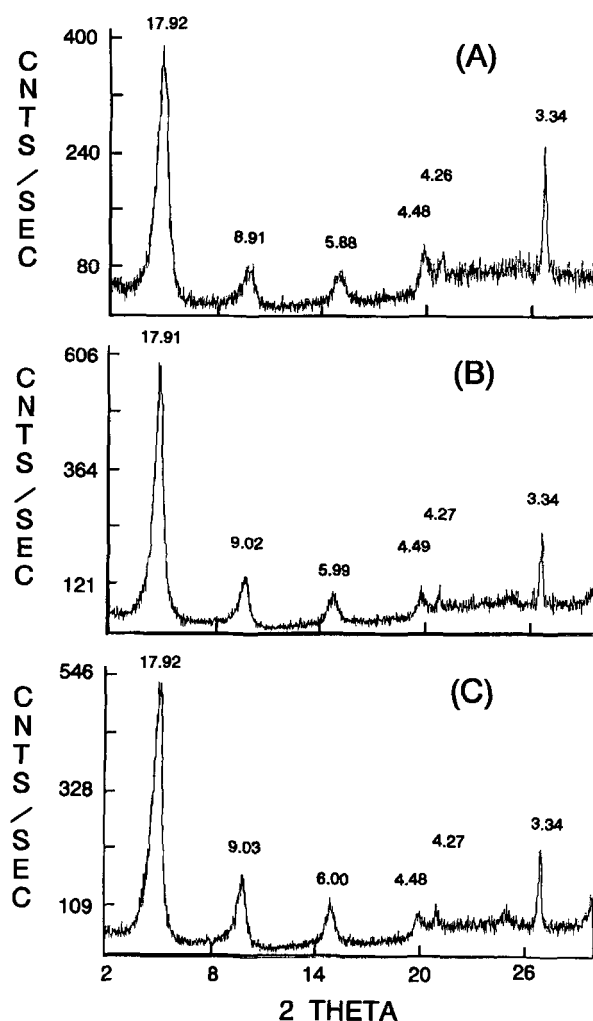


Figure 3. X-ray diffraction patterns of montmorillonite oriented films containing: A) 0.98 meq/g of adsorbed racemic $\text{Ru}(\text{bpy})_3^{2+}$, B) 0.92 meq/g of adsorbed $\Delta\text{-Ru}(\text{bpy})_3^{2+}$, C) 1.00 meq/g of adsorbed $\Delta\text{-Ru}(\text{bpy})_3^{2+}$ (5th points of the adsorption isotherms of Figure 1). The sharp peaks around 3.3 and 4.2 Å are from quartz.

tion is shifted from 9 to 9.5 Å, and the relative intensities of both the second- and third-order reflections are greatly increased.

As previously reported, Figure 5A shows that in the presence of 0.1 M NaCl, the maximum amount of racemic $\text{Ru}(\text{bpy})_3^{2+}$ that can be adsorbed by smectites, is increased to values comparable to those found for the enantiomers (Villemure, 1990). Figure 5B shows that this increased adsorption results in changes in the X-ray diffraction pattern similar to those found for the enantiomers (Figures 4B,C).

Treatment with glycol did not produce any significant changes in the XRD pattern of a film saturated with racemic $\text{Ru}(\text{bpy})_3^{2+}$ (e.g., compare Figures 6A and 3A). However, exposure of films containing enantiomeric $\text{Ru}(\text{bpy})_3^{2+}$ in excess of the clay CEC to glycol,

resulted in a shift of the first peak from 27 Å to approximately 29 Å (Figures 6B,C). The resolution of the first two peaks was improved compared with those shown in Figures 4B,C, but was still incomplete.

Heating a film containing 0.90 meq/g of the racemic cation caused a small shift of the first order reflection, from 17.9 Å at room temperature to 17.3 Å at 300°C. Heating the film to 500°C resulted in the disappearance of all reflections attributed to intercalated $\text{Ru}(\text{bpy})_3^{2+}$. Heating films contained adsorbed $\text{Ru}(\text{bpy})_3^{2+}$ enantiomers in excess of the clay CEC resulted in the gradual disappearance of the 27 Å reflection. Only a shoulder was left after the films were heated to 300°C, and it had completely disappeared from the patterns taken after the films were heated to 500°C. However, the X-ray diffraction patterns of films containing the en-

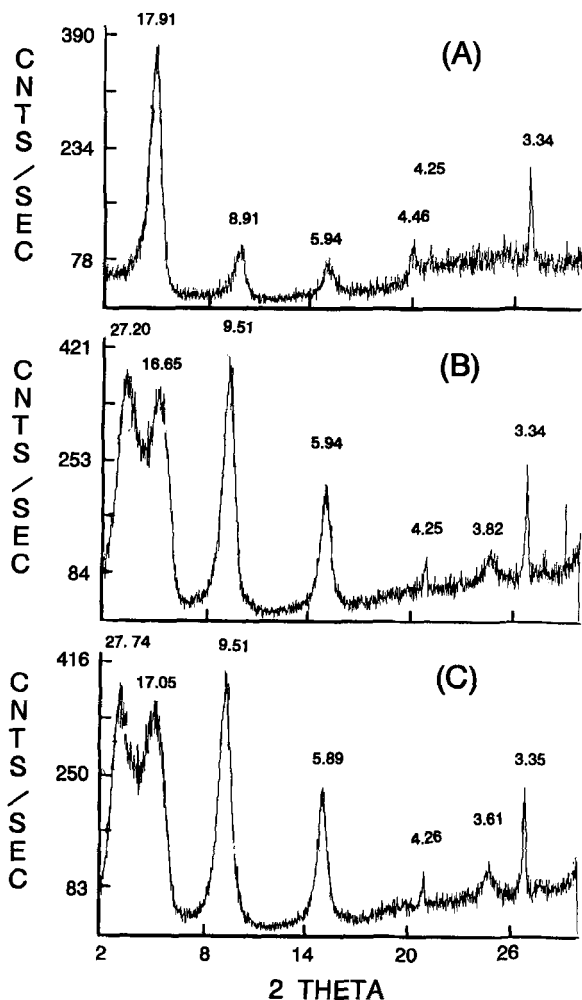


Figure 4. X-ray diffraction patterns of montmorillonite oriented films containing: A) 0.97 meq/g of adsorbed racemic Ru(bpy)₃²⁺ (9th point of the isotherm of Figure 1), B) 1.65 meq/g of adsorbed Δ -Ru(bpy)₃²⁺, C) 1.72 meq/g of adsorbed Δ -Ru(bpy)₃²⁺ (8th points of the isotherms of Figure 1). The sharp peaks around 3.3 and 4.2 Å are from quartz.

antiomeric cations still showed reflections at 18.2, 9.7 and 5.9 Å, attributed to the intercalation of one layer of the cations, even after heating to 500°C.

DISCUSSION

The X-ray diffraction patterns of oriented clay films, partially exchanged with racemic and enantiomeric Ru(bpy)₃²⁺, shown in Figure 2 can be explained by segregation of the adsorbed cations. Segregation is a phenomenon in which cations are selectively adsorbed in some interlayer spaces, rather than being uniformly distributed in all interlayer spaces. It is known to occur for Ru(bpy)₃²⁺ in smectites (Ghosh and Bard, 1984). In fact, it has been invoked to help explain the spectral differences found between clay-adsorbed enantiomeric and racemic Ru(bpy)₃²⁺ at low loading levels (Joshi

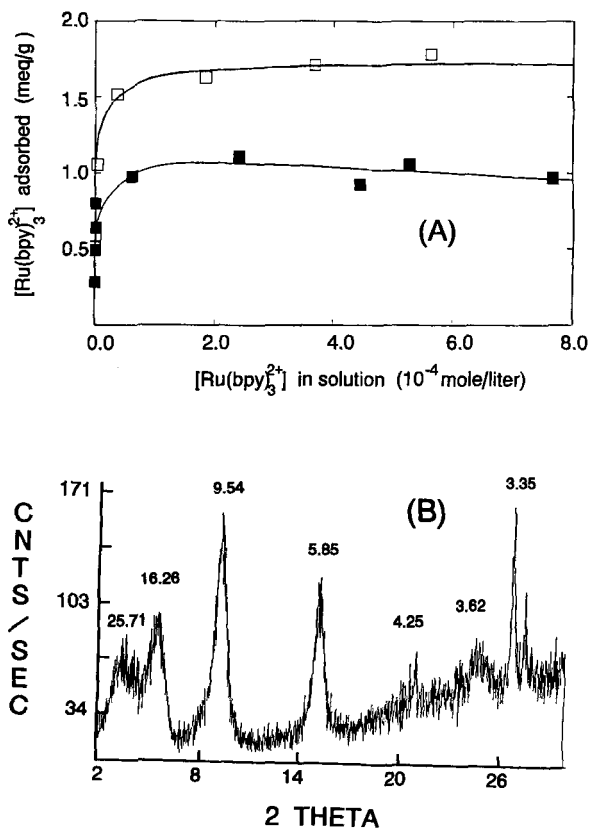


Figure 5. A) Adsorption isotherms of racemic Ru(bpy)₃²⁺ by suspensions of montmorillonite in the absence (filled squares), and in the presence (open squares), of 0.1 M NaCl. B) X-ray diffraction pattern of an oriented film containing 1.71 meq/g of racemic Ru(bpy)₃²⁺ (8th point of the adsorption isotherms). The sharp peaks around 3.3 and 4.2 Å are from quartz.

and Ghosh, 1989). A nonuniform distribution of the adsorbed cations would produce two distinct basal spacings, one for the clay interlayer spaces containing Ru(bpy)₃²⁺ and one for the clay interlayer spaces not containing Ru(bpy)₃²⁺. The X-ray pattern would be the result of the interstratification of these two spacings.

Figure 2 also shows that the first reflection from the clay film partially exchanged with racemic Ru(bpy)₃²⁺ is sharper than those from the films partially exchanged with enantiomeric Ru(bpy)₃²⁺. Although the difference may not be significant, it does suggest that the film exchanged with the racemic mixture was somewhat more ordered than those exchanged with the enantiomers. A possible explanation for this is that the racemic cations, perhaps because of the formation of racemic pairs, were more segregated into fewer interlayer spaces than the enantiomeric cations. A more extensive investigation of films partially exchanged with Ru(bpy)₃²⁺ is needed before we can arrive at firm conclusions.

As expected, Figure 3A shows that a film saturated with racemic Ru(bpy)₃²⁺ produced a series of rational

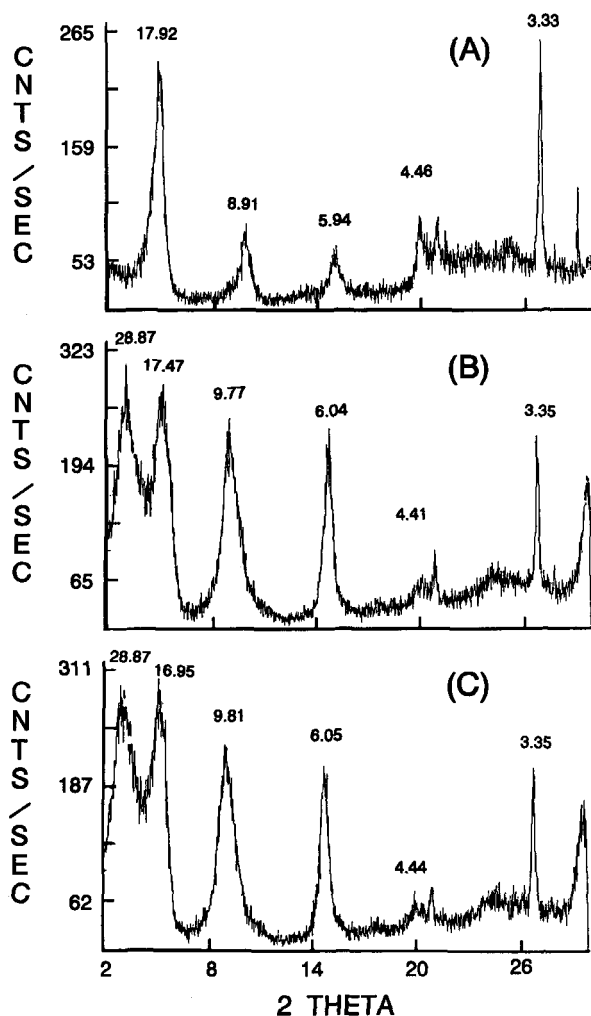


Figure 6. X-ray diffraction patterns of glycolated montmorillonite oriented films containing: A) 0.90 meq/g of adsorbed racemic $\text{Ru}(\text{bpy})_3^{2+}$, B) 1.47 meq/g of adsorbed $\Delta\text{-Ru}(\text{bpy})_3^{2+}$, C) 1.51 meq/g of adsorbed $\Delta\text{-Ru}(\text{bpy})_3^{2+}$. The sharp peaks around 3.3 and 4.2 Å are from quartz.

reflections, giving a basal spacing just under 18 Å (Villemure *et al.*, 1985). The interlayer spacings of 8.3 Å are completely consistent with the intercalation of a single layer of the cation. In light of the differences seen, when less than the clay CEC of $\text{Ru}(\text{bpy})_3^{2+}$ was adsorbed (Figure 2) and, when more than the clay CEC of enantiomeric $\text{Ru}(\text{bpy})_3^{2+}$ was adsorbed (Figure 4), it is interesting that no differences were seen in the XRD patterns of films containing the racemic mixture and the enantiomers when the level of adsorption was close to the clay CEC (see Figures 3B,C).

The most interesting results are those shown in Figure 4. When the films contained enantiomeric $\text{Ru}(\text{bpy})_3^{2+}$ in excess of the clay CEC, an additional reflection appeared at basal spacings of about 27 Å, just about right for the intercalation of 2 layers of

$\text{Ru}(\text{bpy})_3^{2+}$. A reflection corresponding to a similar interlayer spacing was also seen for a film where the addition of NaCl increased the level of adsorption of racemic $\text{Ru}(\text{bpy})_3^{2+}$ to well above the clay CEC (Figure 5).

In hindsight, these results are not all that surprising. As discussed in a previous report (Villemure, 1990), the cross section of a single $\text{Ru}(\text{bpy})_3^{2+}$, based on an L-B monolayer film of a surfactant derivative of this cation, is of the order of 125 Å² (Zhang and Bard, 1989). Therefore, the intercalation of a single layer of $\text{Ru}(\text{bpy})_3^{2+}$, where both faces of the cation are in contact with the clay surface, would require approximately 250 Å²/ion. Figure 1 shows that the films whose X-rays are seen in Figures 4B,C contained approximately 1.7 meq/g of enantiomeric $\text{Ru}(\text{bpy})_3^{2+}$. The crystallographic surface area of this clay, calculated from its unit cell formula (Jaynes and Bigham, 1986) is 740 m²/g. If we assume that only one monolayer of cation was present, the clay surface area available to each adsorbed enantiomer was 140 Å². Thus, there was simply not enough room at the clay surface for the adsorption in a single layer of this much $\text{Ru}(\text{bpy})_3^{2+}$. The same argument can be made for the X-ray spectra shown in Figure 5B. That film contained 1.71 meq/g of racemic $\text{Ru}(\text{bpy})_3^{2+}$.

The shift of the first reflection from around 27 Å to around 29 Å on exposure to glycol can be interpreted as an insertion of a layer, or part of a layer, of glycol molecules between the two $\text{Ru}(\text{bpy})_3^{2+}$ layers. Since the film containing one intercalated layer of racemic cations was unaffected by treatment with glycol (Figure 6), we conclude that the interlayer spaces containing two layers of $\text{Ru}(\text{bpy})_3^{2+}$ cations were easier to expand than those containing a single layer of $\text{Ru}(\text{bpy})_3^{2+}$.

The X-ray pattern of a film containing a single intercalated layer of racemic $\text{Ru}(\text{bpy})_3^{2+}$ was unaffected by heating to 300°C. The loss of all the reflections attributed to intercalated $\text{Ru}(\text{bpy})_3^{2+}$, when the temperature was increased to 500°C is attributed to the destruction of the cation organic bipyridyl ligands. The second intercalated layer of $\text{Ru}(\text{bpy})_3^{2+}$ was less resistant to temperature. The 27 Å reflection was almost completely lost at 300°C. In contrast to the clay-racemic mixture complex, the remaining single intercalated layer of enantiomeric $\text{Ru}(\text{bpy})_3^{2+}$ persisted even after heating the films to 500°C.

CONCLUSIONS

When $\text{Ru}(\text{bpy})_3^{2+}$ is adsorbed in SWy-1 montmorillonite significantly above the clay CEC, the X-ray pattern shows a reflection corresponding to basal spacings of about 27 Å, attributed to the intercalation of 2 layers of the cations. This result is consistent with calculation of the monolayer capacity based on the size of the cations. Although it does not contradict the proposal that the adsorption of racemic $\text{Ru}(\text{bpy})_3^{2+}$ causes

more extensive aggregation of the clay than the adsorption of the enantiomers, this result does not constitute positive evidence for this model. X-ray patterns of oriented films do not necessarily reflect the morphology of the clay suspensions used to prepare the clay films. Films with two layers of intercalated cations could arise either from the stacking of highly-dispersed clay layers covered on both side with a monolayer of the cations, as predicted in our model, or from the stacking of preexisting, doubly-intercalated clay particles. We are pursuing this work to attempt to clarify the mechanism of the formation of the doubly-intercalated films.

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