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## Clay modified electrodes

### Part 10. Studies of clay-adsorbed $\text{Ru}(\text{bpy})_3^{2+}$ enantiomers by UV-visible spectroscopy and cyclic voltammetry

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#### ABSTRACT

The difference of a factor of 2 found in the values of  $c_1$ , the total concentration of adsorbed cation, between racemic  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  and its enantiomers in clay modified electrodes, is attributed to differences in the effect of the adsorption of the cations on the degree of aggregation of the clays. UV-visible spectra indicate less aggregation of the clays upon addition of the enantiomers than the racemate, leaving more exposed surface for the adsorption of the ion pairs. This lower layering explains why the clays were found to adsorb twice their CEC (cation exchange capacity) for the enantiomers, but only their CEC for racemic  $\text{Ru}(\text{bpy})_3^{2+}$ , in contradiction to previous results with  $\text{Ru}(\text{phen})_3^{2+}$ , where it was the racemate that was reported to be adsorbed in excess of the CEC. Despite the differences in the values of  $c_1$ , similar peak currents were found in the cyclic voltammograms of racemic  $\text{Ru}(\text{bpy})_3^{2+}$  and its enantiomers in clay modified electrodes, since a smaller fraction of the adsorbed enantiomers were found to be electroactive. The decrease in currents due to this lower fraction more than makes up for their larger  $c_1$ .

#### INTRODUCTION

This paper centers on the differences in the behavior of  $\text{Ru}(\text{bpy})_3^{2+}$  and its enantiomers on clay modified electrodes. Clay modified electrodes (CME) [1-8] are fabricated by the deposition of a thin clay film on a conductive substrate surface with the aim of utilizing the adsorptive and catalytic properties of clays to provide improved selectivity or sensitivity of the electrode toward solution species. Clays exhibit the same ion exchange properties of other materials that have been used for the modification of electrode surfaces, e.g., Nafion and other polyelectrolytes [9]. In

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addition, they have several advantages over amorphous polymers: low cost, wide availability, higher thermal and chemical stability. They have well-defined layered structures with large surface areas (see refs. 10–12 for discussion of clay minerals and their structure and properties).

Potentially the most important advantage of clays as electrode modifiers is their catalytic properties. A wide variety of chemical conversions can be carried out at clay surfaces, both directly or via incorporation of catalysts [13–17]. In addition to being efficient solid acid catalysts for many organic reactions, the layered structures of clay minerals have been shown to modify the selectivity of some intercalated catalysts [18,19].

Chiral effects on clays have been the subject of a number of studies. For example, in connection with the possible role of clay minerals in the origins of life [20–25], their involvement in the evolution of chirality is the object of some controversy [26–31]. The enantiomers of some optically active metal chelates have been reported to adsorb on clays differently from the racemic mixture. Yamagishi et al., in particular, have published several papers on the interaction of metal chelates with clays [32–36]. They found that smectites, such as montmorillonite and hectorite, adsorbed larger amounts of racemic mixtures of  $M(\text{phen})_3^{2+}$  ( $M = \text{Fe}, \text{Ru}, \text{Ni}$ ; phen = 1,10-phenanthroline) than either of the pure enantiomers. The racemate was found to be adsorbed at twice the clay cation exchange capacity (CEC), while the enantiomers were adsorbed only to the clay CEC. It was postulated that in smectites these cations were adsorbed in racemic pairs, which were assumed to pack more efficiently than enantiomeric pairs. It was therefore possible to intercalate more cations in the limited space available between the clay layers for the racemate than for the enantiomers. Thus, only half as much of the pure enantiomers could be adsorbed, since these pairs could not be formed [32–36].

In previous studies of the modification of electrode surfaces with clay films, the interaction of  $\text{Ru}(\text{bpy})_3^{2+}$  with CME has been extensively investigated [37–41]. We were intrigued by previous reports showing chiral effects, especially those dealing with asymmetric electrochemical oxidation of  $\text{Co}(\text{phen})_3^{2+}$  [42] and sulfides [43] with electrodes prepared by soaking a clay film in  $\Lambda\text{-Ru}(\text{phen})_3^{2+}$ , and so we undertook an investigation of the electrochemical and spectroscopic properties of CME exchanged with racemic  $\text{Ru}(\text{bpy})_3^{2+}$  and its two enantiomers, with a view towards their use in asymmetric electrochemical reactions.

## EXPERIMENTAL

### *Materials*

The clays used were montmorillonites, (STx-1) from Gonzales County, TX, and (SWy-1) from Crook County, WY; a nontronite (SWa-1, Ferruginous smectite) from Grant County, WA; and a hectorite (SHCa-1) from San Bernadino County, CA. They were obtained from the Source Clay Minerals Repository (University of Missouri, Columbia, MO). The sodium forms of the clays were prepared and the < 0.2 mm fractions separated by literature procedures [44,45]. Briefly, the clays



were stirred in 1 M NaCl for 48 h to convert them to the sodium form. After centrifugation and washing with water, they were dialyzed through a Spectrapor membrane until a negative chloride test was obtained. The  $< 0.2 \mu\text{m}$  fractions were then separated by centrifugation (Beckman, Model J2-21) at 5000 rpm for 25 min. The sediments were finally freeze-dried. In the case of hectorite, the clay was contaminated by carbonate, which was destroyed by acidification of a suspension to pH 3.5 prior to the NaCl treatment. Excess non-structural iron in the nontronite was removed by treatment with dithionite and citrate [46].

$\text{Ru}(\text{bpy})_3^{2+}$  (Aldrich Chemicals, Milwaukee, WI) was used without further purification. The enantiomers were separated by treatment with potassium antimony tartrate (Aldrich), according to a literature procedure [47]. They were isolated as the iodides. After two recrystallizations, the measured optical rotations were  $[\Phi]_D = -7300^\circ$  for the  $\Delta$  isomer and  $+6700^\circ$  for the  $\Lambda$  isomer, (literature,  $-7184^\circ$  and  $+7194^\circ$ , respectively [47]). The chlorides were prepared by stirring solutions of the iodides with AgCl.

#### *Preparation of the electrodes*

The clay modified electrodes were prepared by spin coating. The supports were  $1 \times 2$  cm pieces of indium-doped  $\text{SnO}_2$  coated glass (Delta Technologies, Stillwater, MN), cleaned by three cycles of sonication in EtOH. One drop of  $\text{H}_2\text{SO}_4$  (10% v/v) was added to a 10 g/l suspension of the clay in distilled water to make a low viscosity gel. Positive indication of the formation of the gel was that even after standing several days undisturbed, there was no sign of sedimentation. Without this  $\text{H}_2\text{SO}_4$  treatment, films could not be made by spin coating. The clay suspension did not wet the hydrophobic supports. Drops of the clay gel were spin coated at 3000 rpm (Headway Research, Garland, TX). This gave films with interference colors of purple to yellow. Part of the films were then rubbed off to give  $1 \text{ cm}^2$  electrodes. The thickness of the film before and after soaking in  $\text{Ru}(\text{bpy})_3^{2+}$  was measured on a profilometer (Sloan Dektak FLM, Santa Barbara, CA). Films used for the determination of the adsorption isotherms of Fig. 2 were prepared by evaporation of a known volume ( $0.10 \text{ cm}^3$ ) of a montmorillonite suspension of known concentration (3.0 g/l) to produce  $1 \text{ cm}^2$  films, ca.  $1 \mu\text{m}$  thick.

#### *Methods and equipment*

The clay modified electrodes were soaked in 0.100 mM  $\Delta$ ,  $\Lambda$  or racemic  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  for 20 h. In some cases, the amount of cation adsorbed by each film was determined by measuring the concentration of cations left in the soaking solutions. In these cases the volumes of the soaking solutions were chosen such that the adsorption would cause decreases of between 15 and 35% in the amount of  $\text{Ru}(\text{bpy})_3^{2+}$  in solution. The UV-visible absorption spectra were measured on a Hewlett-Packard Model 8451A spectrophotometer (Avondale, PA). To measure the adsorption isotherms, suspensions of the clays were mixed with solutions of the cations. After 48 h the mixtures were centrifuged, and the decrease in the concentra-



tion of  $\text{Ru}(\text{bpy})_3^{2+}$  in the supernatants was determined by UV-visible spectroscopy (MLCT band,  $\lambda_{\text{max}} = 452 \text{ nm}$ ,  $\epsilon = 14600 \text{ M}^{-1} \text{ cm}^{-1}$  [48]).

Cyclic voltammetry experiments were performed with a Princeton Applied Research (PAR, Princeton, NJ) Model 175 universal programmer and a Model 173 potentiostat. All electrochemical experiments were done in an undivided three-electrode cell. The counter electrode was Pt gauze and the reference electrode was saturated calomel electrode (SCE). The solutions were degassed by bubbling  $\text{N}_2$  prior to the measurements.

## RESULTS

### UV-visible spectroscopy

Figure 1 shows the adsorption isotherms of racemic  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  and its enantiomers by suspensions of hectorite. These were measured spectrophotometrically by determining the decrease in  $\text{Ru}(\text{bpy})_3^{2+}$  concentration in the supernatant after 48 h. The clay adsorbed more of the pure enantiomers than the racemate. In the case of the racemic mixture, one equivalent of cation was adsorbed, compared to almost two equivalents of the pure enantiomers. Similar results were found for montmorillonite. Films of the two clays were also found to adsorb more of the pure enantiomers than of the racemic mixture (Fig. 2). These results are different from those reported for  $\text{Ru}(\text{phen})_3^{2+}$ , where clay minerals adsorbed two equivalents of racemic mixture but only one of its enantiomers [32]. The isotherms were also affected by the nature of the counter anions.  $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$  and its enantiomers behaved like the chlorides (Fig. 3a), but there was very little difference between racemic  $\text{Ru}(\text{bpy})_3\text{I}_2$  and its enantiomers (Fig. 3b).

The UV-visible spectra of racemic  $\text{Ru}(\text{bpy})_3^{2+}$  and its enantiomers in clay suspensions were also measured (Figs. 4 and 5). As previously reported [49],

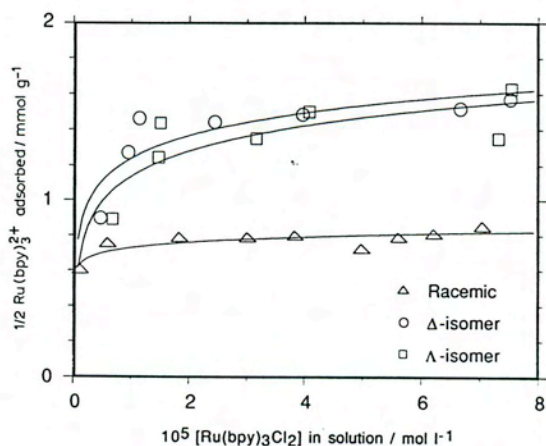


Fig. 1. Adsorption isotherm of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  and its enantiomers by hectorite (SHCa-1) suspensions.



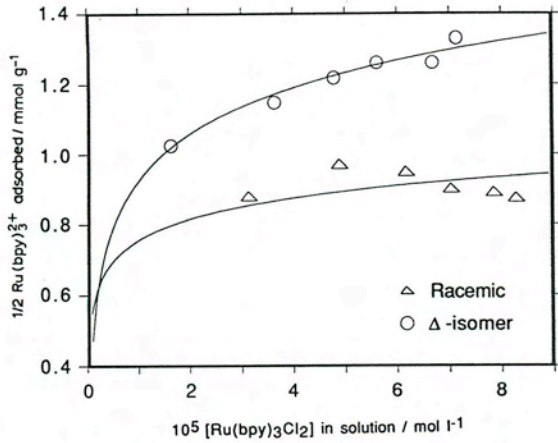


Fig. 2. Adsorption isotherms of racemic and  $\Delta$ - $\text{Ru}(\text{bpy})_3\text{Cl}_2$  by films of montmorillonite (SWy-1). Films were  $1 \text{ cm}^2$  and ca.  $1 \text{ mm}$  thick (see Experimental).

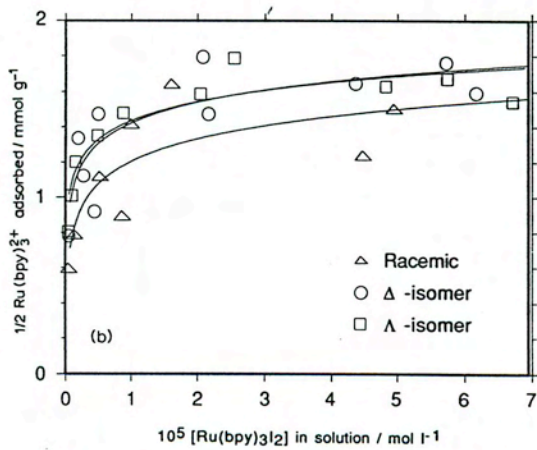
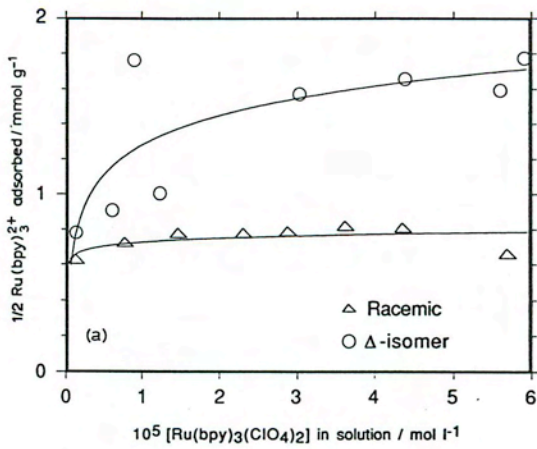


Fig. 3. Comparison of the adsorption isotherms of  $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$  and  $\text{Ru}(\text{bpy})_3\text{I}_2$  and their enanti-



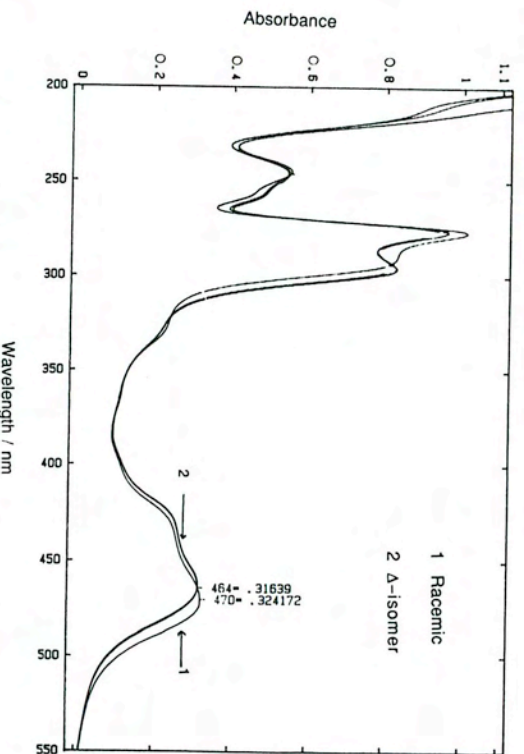


Fig. 4. UV-visible absorbance spectra of racemic and  $\Delta$ -Ru(bpy) $_3^{2+}$ ,  $2.0 \times 10^{-5}$  M in 0.50 g/L hectorite (SHCa-1) (ca. 10% CEC).

differences were seen between the racemic mixture and the enantiomers. The MLCT band was shifted from 452 nm in water to 470 nm in hectorite for the racemate, but only to 464 nm for the enantiomers. Also, the 288 nm band in water was split into two lower intensity bands at 276 and 296 nm for the enantiomers, while for the racemic mixture, the second band appeared only as a shoulder.

The same differences were seen in montmorillonite (STx-1) (Fig. 5). Further, in this case, it was noted that these differences were time dependent. Figure 5a shows the spectra of racemic and  $\Delta$ -Ru(bpy) $_3^{2+}$  in montmorillonite 1 h after the mixing of the cations and the clay. The MLCT band maxima were at 466 nm in both cases, while the 288 nm band was split for the enantiomer but not for the racemate. Fifteen hours later the  $\Delta$ -isomer spectrum was unchanged (Fig. 5b), but for the racemic mixture, the MLCT band had shifted to 472 nm and its intensity increased from 0.386 to 0.410. The 288 nm band was more clearly split. Finally, the variation of the spectra with cation-to-clay ratio was studied. As the loading of the clay decreased, the MLCT band shifted to the red and increased in intensity. The splitting of the 288 nm band also became more pronounced.

#### Cyclic voltammetry

In Fig. 6, the cyclic voltammograms of two sets of montmorillonite (SWy-1) electrodes soaked 20 h in solutions of  $\Delta$ ,  $\Lambda$ , and racemic Ru(bpy) $_3^{2+}$  are compared. The relative peak currents observed for the racemate and its enantiomers were very variable from one set of electrodes to another. Results of Fig. 6 represent the two extremes in observed behavior. The two sets of electrodes were prepared from the same suspension and were soaked in aliquots of the same solutions of cations for the



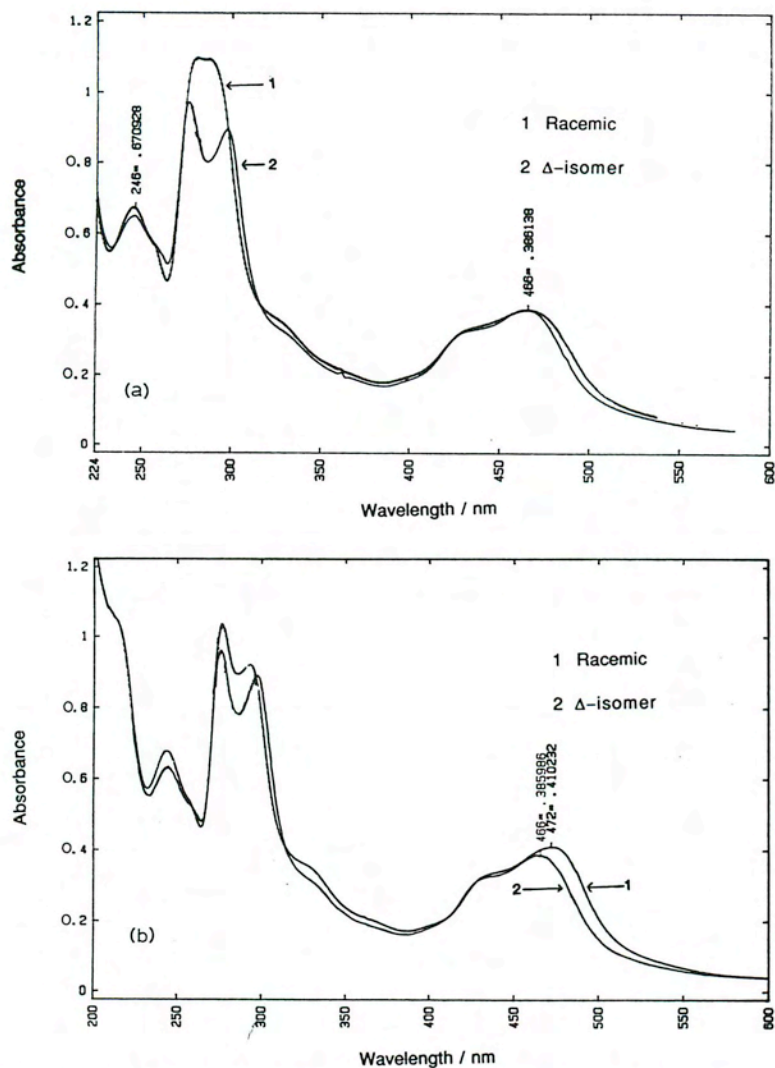


Fig. 5. UV-visible absorbance spectra of racemic and  $\Delta$ - $\text{Ru}(\text{bpy})_3^{2+}$ ,  $2.0 \times 10^{-5}$  M in 0.50 g/l montmorillonite (STx-1) (ca. 10% CEC). (a) 1 h; (b) 15 h after mixing of the cation and the clay.

same period of time. Yet, in Fig. 6a, the voltammograms of the two enantiomers are practically identical to that of the racemate, while in Fig. 6b the peak currents of the enantiomers are only about 60% that of the racemate.

This variability of the relative peak currents of the racemate and its enantiomers was very typical. Fifteen sets of electrodes were measured. In general, the enantiomers gave somewhat smaller currents,  $80 \pm 20\%$  of those of the racemate (see Table 1). Similar results were obtained with electrodes coated with hectorite or nontronite



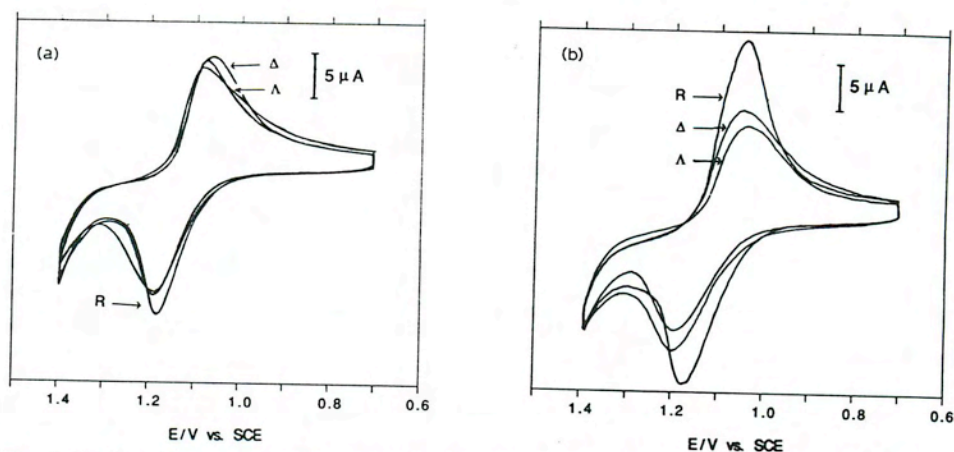


Fig. 6. Cyclic voltammograms of montmorillonite (SWy-1) electrodes soaked in 0.100 mM  $\Delta$ ,  $\Lambda$ , or racemic  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  for 20 h. Current ratio (a) ca. 1; (b) 0.6 taken in 0.1 M  $\text{Na}_2\text{SO}_4$  at 100 mV/s.

films, except for the larger magnitude of the currents, especially in the case of nontronite (see Table 2). This variability in relative responses of the racemate and the enantiomer can be traced to several factors, as discussed below. These include the fact that only a small fraction of the incorporated  $\text{Ru}(\text{bpy})_3^{2+}$  is electroactive and that the clay particle structure is affected differently by adsorption of the different forms.

Despite this wide variability, the peak currents of the adsorbed enantiomers cannot be considered to be significantly different from those of the adsorbed racemic mixture. Certainly, the enantiomers did not give twice the current of the racemic mixture, as could have been expected from the differences in the adsorption isotherms. It is known that only a small fraction of the cations adsorbed in a clay modified electrode is electroactive [8,37,40,41]. We therefore decided to look more closely at the relation of the peak currents with  $c_1$ , and with  $c^*$ , the concentration of electroactive species.

To obtain reliable values of  $c_1$ , the total amount of  $\text{Ru}(\text{bpy})_3^{2+}$  adsorbed by the clay film, the decrease in concentration of  $\text{Ru}(\text{bpy})_3^{2+}$  in the soaking solutions was

TABLE 1

Summary of CV studies of montmorillonite (SWy-1) coated tin oxide electrodes with incorporated  $\text{Ru}(\text{bpy})_3^{2+}$  <sup>a</sup>

Cation	$i_{pc}/\mu\text{A}$	$E_{pc}/\text{V}$	$i_{pa}/\mu\text{A}$	$E_{pa}/\text{V}$
Racemic	$13.9 \pm 4.2$	1.05	$15.5 \pm 3.9$	1.14
$\Delta$ -isomer	$9.8 \pm 4.8$	1.06	$12.4 \pm 5.2$	1.17
$\Lambda$ -isomer	$11.0 \pm 3.2$	1.05	$13.1 \pm 3.2$	1.16

<sup>a</sup> Averages of 15 sets of results. The standard deviations of the averages are shown. Voltammograms obtained in 0.1 M  $\text{Na}_2\text{SO}_4$  at 100 mV/s.



TABLE 2

Results of cyclic voltammetry for  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  and its enantiomers adsorbed on hectorite (SHCa-1) and nontronite (SWa-1). Recorded in 0.1 M  $\text{Na}_2\text{SO}_4$  at 100 mV/s. (For nontronite, averages of two sets of electrodes)

Cation	Clay	$I_{pc}/\mu\text{A}$	$E_{pc}/\text{V}$	$i_{pa}/\mu\text{A}$	$E_{pa}/\text{V}$
Racemic	hectorite	20.0	1.08	19	1.15
$\Delta$ -isomer	hectorite	14.5	1.08	17	1.15
$\Lambda$ -isomer	hectorite	16.5	1.08	14	1.15
Racemic	nontronite	52	1.02	44	1.12
$\Delta$ -isomer	nontronite	39	1.00	30.5	1.13
$\Lambda$ -isomer	nontronite	38	1.01	32.3	1.13

measured spectrophotometrically before and after adsorption. This decrease varied between 15 and 35% of the amount of cation initially present.  $c_t$  could then be calculated using the film thickness, measured by profilometry, and the electrode area. Figure 7a shows the cyclic voltammograms of a set of montmorillonite electrodes for which this was done. In this case the waves were practically identical for the three electrodes. They were reversible at scan rates of less than 50 mV/s. Peak currents as a function of  $v^{1/2}$  are plotted in Fig. 7b. The values of  $c_t$  calculated in this way are shown in Table 3. Note that  $c_t$  values could also be obtained from the adsorption maxima of the films themselves (see inset, Fig. 7a). These were not in agreement with those determined by monitoring the decrease in concentration of the soaking solutions. They were not considered as reliable for reasons discussed below.

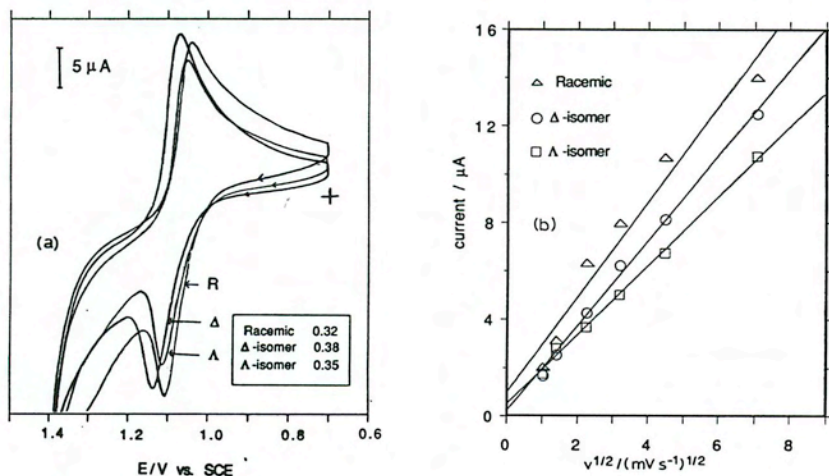


Fig. 7. (a) Cyclic voltammograms of a set of montmorillonite (STx-1) electrodes, 200 nm thick (before) and 300 nm thick (after) soaking in 0.1 mM  $\Delta$ -,  $\Lambda$ -, or racemic  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ . Inset: absorption maxima. (b) Current vs. (scan rate) $^{1/2}$ . 0.2 M  $\text{Na}_2\text{SO}_4$  at 100 mV/s.



TABLE 3

Determination of the fraction of electroactive cation. Electrodes were prepared by spin coating a fresh suspension of montmorillonite (STx-1)

Cation adsorbed	$10^8 \times \text{amount}/\text{mol}^a$	$10^5 \times \text{volume}/\text{cm}^3^b$	$10^4 c_t/\text{mol cm}^{-3}$	$10^5 c^*/\text{mol cm}^{-3}^c$	$c^*/c_t$
Racemic	3.16	3.45	9.2	6.2	0.067
$\Delta$ -enantiomer	5.81	3.60	16.1	5.0	0.031
$\Lambda$ -enantiomer	5.02	3.30	15.2	5.8	0.038

<sup>a</sup> From the decrease in concentration of the soaking solutions.

<sup>b</sup> From the thickness of the films, 300 nm.

<sup>c</sup> From the currents at 1 mV/s.

At low scan rates ( $< 5$  mV/s), the cathodic waves were almost symmetrical, as typical of thin layer behavior. From  $i_{pc}$  at 1 mV/s, approximate values of  $c^*$ , the concentration of electroactive species, were calculated (see Table 3). The ratio  $c^*/c_t$  could then be obtained. Also, for this set of electrodes, the peak current decreased with time. This was attributed to leaching of the adsorbed cations by the electrolyte. The currents decreased from 19 to 14  $\mu\text{A}$  for the racemate and from 19 to 17  $\mu\text{A}$  for the enantiomers after 90 min of holding films in the electrolyte solutions.

Further evidence of the importance of film structures on the currents is given by the comparison of the results of Table 3 with those for a different set of electrodes prepared from a suspension that had been aged for 6 months (Table 4). Although the values of  $c_t$  and  $c^*$  are different, the ratios  $c^*/c_t$  are remarkably similar. Aside from the ages of the suspensions used for their preparation, the main difference between the two sets of electrodes was that those of Table 4 were almost twice as thick 570 vs. 300 nm, as those of Table 3. As discussed below, these factors are expected to affect the structures of the films.

Figure 8 shows the growth of the peak currents of montmorillonite (SWy-1) electrodes as a function of soaking time. The wave increased more rapidly for the racemate than for the enantiomers. Plateaus were reached after 2 h in the  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  solutions, at which point in this trial the current for the racemic

TABLE 4

Determination of the fraction of electroactive cation for a set of electrodes 570 nm thick, prepared by spin coating a six-month old suspension of montmorillonite (STx-1)

Cation adsorbed	$10^8 \times \text{amount}/\text{mol}^a$	$10^4 c_t/\text{mol cm}^{-3}$	$10^5 c^*/\text{mol cm}^{-3}^b$	$c^*/c_t$
Racemic	6.47	8.6	5.2	0.061
$\Delta$ -enantiomer	6.49	8.6	2.8	0.032
$\Lambda$ -enantiomer	7.11	9.5	2.8	0.029

<sup>a</sup> From the decrease in concentration of the soaking solutions.

<sup>b</sup> From the currents at 1 mV/s.



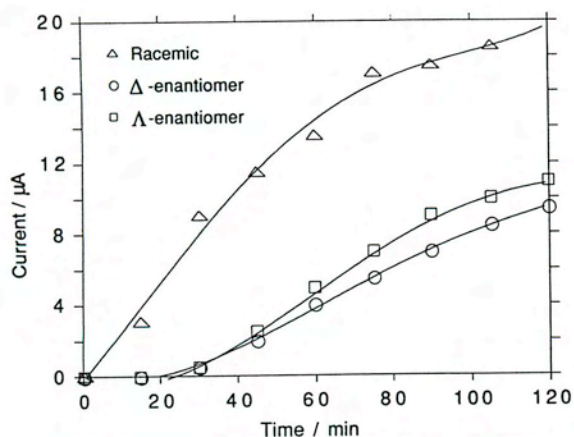


Fig. 8. Peak current as a function of soaking time, for montmorillonite (SWy-1) electrodes. 0.1 M  $\text{Na}_2\text{SO}_4$  at 100 mV/s, in the presence of 0.100 mM  $\Delta$ -,  $\Lambda$ -, or racemic  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ .

electrode was twice that of the enantiomers.  $E_{1/2}$  values also varied with soaking time. After 30 min in the solutions, they were 1.040 V for all three electrodes. After 2 h they had increased by about 50 mV, and after 24 h, by 90 mV. This shift has been attributed in similar experiments with  $\text{Cr}(\text{bpy})_3^{3+}$  to a decrease in the average distance between the adsorbed cations, and therefore, an increase electrostatic repulsion, with increased concentration of adsorbed cation [50].

## DISCUSSION

### UV-visible spectroscopy

The examination of the adsorption isotherms of Figs. 1–3 poses two questions. First, given that clays are achiral, how can we account for the difference in the extent of adsorption of racemic  $\text{Ru}(\text{bpy})_3^{2+}$  and its two enantiomers? Second, how can we reconcile these results with those reported for other metal chelate cations of this type, in particular  $\text{Ru}(\text{phen})_3^{2+}$ , and the racemic pairs adsorption model developed to explain them?

Figures 1 and 2 show clear differences in the extent of adsorption of racemic,  $\Lambda$ - and  $\Delta$ - $\text{Ru}(\text{bpy})_3^{2+}$  by hectorite and montmorillonite. However, the results are different from those that were expected in the light of the reported behavior of  $\text{Ru}(\text{phen})_3^{2+}$  [33]. For the latter, it is the racemic mixture that was adsorbed to twice the clay CEC, while the optical isomers were only adsorbed up to the CEC, the opposite situation of that seen in Fig. 1. Since these two cations have such similar structures, how can we account for this difference?

One possibility is that clay minerals can still discriminate between the two cations, despite their similarity of structure. The 1,10-phenanthroline ligand is more rigid than the bipyridyl ligand. This rigidity may affect the efficiency of packing, which is the key to the racemic pairs model. There is prior evidence of differences in



the interactions of these two cations with smectite clays. For example, while the luminescence intensity of racemic  $\text{Ru}(\text{bpy})_3^{2+}$  adsorbed in a hectorite suspension is twice that of adsorbed  $\Delta$ - or  $\Lambda$ - $\text{Ru}(\text{bpy})_3^{2+}$  [49], the opposite is true for adsorbed  $\text{Ru}(\text{phen})_3^{2+}$  [51]. Another example of very different behavior of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{phen})_3^{2+}$  pertains to their interaction with DNA [52,53].  $\text{Ru}(\text{phen})_3^{2+}$  intercalates between the bases of double-stranded DNA, while  $\text{Ru}(\text{bpy})_3^{2+}$  does not. Moreover, the interaction of  $\text{Ru}(\text{phen})_3^{2+}$  is different for the different optical isomers, because of "packing" considerations of the non-intercalated ligands within the groove of the right-handed helix of DNA [52,53].

The effect of the counter anion was also not investigated separately in previous studies [32–36]. It is known that the counter anion affects the adsorption isotherm of racemic  $\text{Ru}(\text{bpy})_3^{2+}$  by clays [54]. Cations of this type can shield their counter ions from the negative charges of the clays, resulting in adsorption of ion pairs in excess of the clay CEC. For instance, while racemic  $\text{Fe}(\text{bpy})_3\text{Cl}_2$  is reported to be adsorbed only to the CEC of hectorite,  $\text{Fe}(\text{bpy})_3\text{SO}_4$  is adsorbed to more than the CEC [54]. The effect of the counter anion on the adsorption isotherms is shown clearly here in the differences between  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  and  $\text{Ru}(\text{bpy})_3\text{I}_2$  (Figs. 1 and 3b). There is also a problem with the use of  $\Delta A$  at 480 nm for the determination of the amount of  $\text{Ru}(\text{phen})_3^{2+}$  adsorbed by a clay. The MLCT band of this cation is shifted to a different extent for the racemate, than for the enantiomers [49]. This difference in red shift was also seen here for  $\text{Ru}(\text{bpy})_3^{2+}$  (Figs. 4 and 5). This larger shift may explain the faster rise of  $\Delta A$  at 480 nm found for the racemate, especially at low loading levels [34].

In attempting to reconcile our results with the racemic pairs adsorption hypothesis, let us look at the basis of this model. Surprisingly, it is a selective adsorption due to the efficiency of packing of the cations in the clay basal planes. Clays have a lamellar structure. Therefore, a selectivity based on the thickness of the adsorbates may be expected. There are several reports of selectivity of this type, called segregation by clays [54–56]. Selectivity within the basal planes is, however, unexpected. One would not expect the gallery spaces of clay particles to have specific adsorption sites sufficiently defined to cause a factor 2 in the extent of adsorption. At most, small differences in packing efficiency should result in small differences in the amount of cation adsorbed.

But, because of a correspondence between the sizes of the  $\text{Ru}(\text{bpy})_3^{2+}$  cation and the surface charge densities of the clay used, there is a mechanism by which small differences in the packing efficiencies could result in differences of close to a factor 2 in the adsorption isotherms. One can extend the racemic pairs adsorption model by taking account of the effect of the degree of aggregation of the clay particles on the surface area available for the adsorption of cations.

We propose that the adsorption of racemic  $\text{Ru}(\text{bpy})_3^{2+}$  results in more extensive aggregation of the clay than does adsorption of the enantiomers. In Fig. 9, the effect of the particle aggregation on the surface area available for adsorption is represented schematically. At one extreme is a degree of aggregation of 1. The clay is totally dispersed. The particles are composed of isolated layers. Cations can be



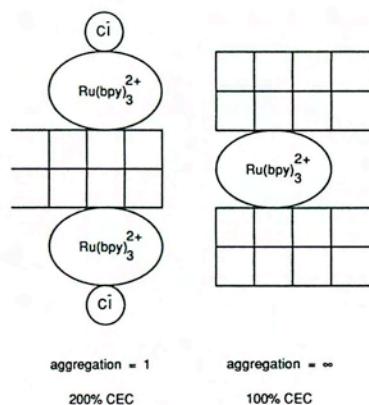


Fig. 9. Schematic representation of an intercalated and a surface adsorbed  $\text{Ru}(\text{bpy})_3^{2+}$  cation. Each square in the clay layer represents a unit cell.

adsorbed on both sides. The other extreme is an infinite aggregation. All the clay layers are in a single stack. Cations are mainly adsorbed between two layers, so that only half as much can be adsorbed.

This more extensive layering of the clay suspensions containing the racemic mixture is supported by the differences seen in the absorption spectra (Figs. 4 and 5). In essence, two differences were seen between the spectra of the racemic mixture and the pure enantiomers in the presence of the clays, first, a larger red shift of the MLCT band of the racemate and second, a more extensive splitting of the 288 nm  $\pi-\pi^*$  band for the enantiomers. Both of these differences have been shown to be an indication of more extensive intercalation of the racemate as opposed to adsorption on the external surfaces of the clays [57–60].

Further support for the attribution of these spectral differences to aggregation of the clay is provided by the time dependence shown in Fig. 5. It takes time for rearrangement of the clay particles to take place. As a result, for the racemate, soon after the mixing of the cation and the clay, the red shift of the MLCT band is smaller, and identical to that of the  $\Delta$ -isomer (Fig. 5a). But, after 15 h, when aggregation of the clay layers has had time to occur, a larger shift results. Since this increase in shift with time was not found for the enantiomers, it can be assumed that aggregation did not take place or, at least, was not as extensive.

This is also supported by the apparent shift of the MLCT band with decrease of the cation-to-clay ratio. In these experiments the concentration of the cation was kept constant. To reduce the loading, the clay concentrations were increased, resulting in more layering and therefore larger red shifts. In support of the above interpretation is a recent report of larger red shifts of the MLCT band of  $\text{Ru}(\text{bpy})_3^{2+}$  in water with an increase in concentration [61]. The larger red shift found here for the more aggregated clay containing the racemate can be taken as an indication of a larger local concentration of intercalated cations compared to those adsorbed on the external surfaces.



To understand why adsorption of the racemic mixtures causes more aggregation than the adsorption of the enantiomers, one returns to the racemic pair adsorption hypothesis. A comparison of the sizes of the  $\text{Ru}(\text{bpy})_3^{2+}$  cation with the surface charge density of the clay shows how small differences in the packing efficiency can result in such an important difference in the extent of layering of the clay. As shown in Fig. 9, each intercalated  $\text{Ru}(\text{bpy})_3^{2+}$  covers approximately 3 clay unit cells,  $3/2$  units on each side. With a CEC of 0.85 mmol univalent cation/g, Na-montmorillonite has an average unit cell charge of  $-0.62$ . It therefore takes about 3.25 unit cells to compensate for the  $2+$  charge of a  $\text{Ru}(\text{bpy})_3^{2+}$  cation intercalated between two layers of an aggregated clay. Therefore, to allow the clay to be saturated with this cation and be aggregated, the packing must be efficient. In line with the racemic pair-adsorption model, this packing is efficient for the adsorbed racemic mixture, but not for the adsorbed enantiomers. Adsorption of the enantiomers therefore produces a clay with a lower degree of aggregation. This leaves more exposed external surface. Since cations of this type can shield their counter anion from the clay negative charges, this extra surface allows the adsorption of cation-anion pairs in excess of the CEC. Paradoxically, a more efficient packing of the racemic mixture results in adsorption of larger amounts of the enantiomers.

Attempts to measure directly the degree of aggregation of the clay suspensions containing the various forms of the cation by measuring either their turbidity or their viscosity were unsuccessful. Variations were too small to be significant, probably because it was necessary to work at very low loading levels in order to avoid flocculation of the clays. Moreover, the viscosity and turbidity measurements will provide a reliable indication of the degree of aggregation (i.e., ratio of major to minor axis) only if there is no change in the particle shapes. We have evidence that this may not be the case here. SEM of clay particles partially exchanged with  $\text{Ru}(\text{bpy})_3^{2+}$  shows the formation of large globular aggregates [62].

#### *Cyclic voltammograms*

The results of the cyclic voltammetry of clay modified electrodes soaked in racemic  $\text{Ru}(\text{bpy})_3^{2+}$  and its enantiomers would initially appear to be in disagreement with the adsorption isotherms of Figs. 1 to 3. The currents of electrodes containing the enantiomers are not significantly larger than those containing the racemic mixture. If anything, although there are wide variations in the relative peak currents, it is the currents of the racemic mixtures that would appear somewhat larger (Fig. 6 and Table 1).

The electrodes are, of course, modified with clay films, while most of the UV-visible measurements were done on clay suspensions. With clays, one must always be cautious about comparing results from two different states. The effect of the degree of aggregation of the clay on the extent of adsorption of the different forms of  $\text{Ru}(\text{bpy})_3^{2+}$ , shown schematically in Fig. 9, is easier to envisage for suspensions than for films. However, we do not believe that this change in the clay state is the sole explanation of the differences between the voltammetric and the spectroscopic results. Figure 2 shows that we also had more extensive adsorption of



the enantiomers by clay films, even if the differences were not as large. Rather, we believe that this was due to differences in  $c^*/c_t$ , the fraction of adsorbed cations that were electroactive. To test this hypothesis requires separate measurements of  $c^*$ , the electroactive concentration and  $c_t$ , the total concentrations of adsorbed cation.

The first problem was obtaining good values of the total amount of  $\text{Ru}(\text{bpy})_3^{2+}$  adsorbed by a given electrode. Simply measuring the absorbance of the films proved inadequate. Concentrations of adsorbed cations measured in this way were not in agreement with those obtained by monitoring the decrease in concentrations of cation in the soaking solutions. For example, the absorbance of the electrodes of Fig. 7 (see inset), gave  $c_t$  values of 4.9, 5.8, and  $5.3 \times 10^{-4} \text{ mol/cm}^3$  for racemic,  $\Delta$ -, and  $\Lambda$ - $\text{Ru}(\text{bpy})_3^{2+}$ , which were not in agreement with those of Table 3. There are two possible explanations for these discrepancies. The first pertains to the molar extinction coefficient of the cation adsorbed in clays. As mentioned previously, the apparent intensity of the MLCT band depends on the extent of loading of the clays. The value of  $\epsilon$  used in these calculations was  $21000 \text{ M}^{-1} \text{ cm}^{-1}$ , reported for a loading of 5% of the CEC [56]. A lower value of  $\epsilon$  gave values of  $c_t$  closer to those of Table 3; however,  $c_t$  for the adsorbed enantiomers was still not that much larger than that of the racemic mixture. The second explanation is that Beer's law is no longer obeyed at the high local concentrations of the intercalated cations. Local concentrations of  $\text{Ru}(\text{bpy})_3^{2+}$  in the clay films were of the order of 1 M for the racemate and even larger for the pure enantiomers. Since a larger proportion of the space in the films was actually taken by the clay layers, the relative distances between cations were very small. For the surface area,  $750 \text{ m}^2/\text{g}$ , and a CEC of 0.85 mmol univalent cation/g, at 100% CEC, the area available for each cation is  $1.46 \text{ nm}^2$ . This represents rather tight packing of the ions, since with an L-B monolayer film of a  $\text{Ru}(\text{bpy})_3^{2+}$ -based surfactant, the pressure started to rise at an area of  $1.25 \text{ nm}^2/\text{molecule}$  [63].

Such problems were not encountered when  $c_t$  was evaluated from the decrease in the concentration of the cation in the soaking solution. There the main uncertainty was on the exact volumes of the films. Because of surface irregularities, values of the film thicknesses determined by profilometry were accurate only to  $\pm 10\%$ . Note that the values of  $c^*/c_t$  are more reliable than either  $c_t$  or  $c^*$ , since the volumes of the films cancel in the ratios.

The results in Tables 3 and 4 show that only a very small fraction of the adsorbed cations was electroactive. The fraction of incorporated  $\text{Ru}(\text{bpy})_3^{2+}$  that was electroactive was about twice as large for the racemate as for either enantiomer. The measured currents are a function of  $c^*$ , not  $c_t$ . Variations in the ratio  $c^*/c_t$  account for the differences between the spectroscopic and voltammetric results. Two factors work in opposite directions. The larger  $c^*/c_t$  of the racemic mixture more than makes up for the larger  $c_t$  of the enantiomers, resulting in little or no difference in the CV peak currents. For the same reason, the curves of Fig. 8 are not a reliable measure of the amount of cation adsorbed. What is measured is the growth of  $c^*$ , not  $c_t$ .



Since the  $c^*/c_1$  ratios are so small, relatively small variations in  $c^*$  can have a large effect on the observed currents. This explains the wide variability of the relative currents seen in Table 1. Furthermore, the currents are still indirectly related to  $c_1$ . Factors that affect the degree of aggregation of the clay, and therefore  $c_1$ , will result in fluctuations in the observed currents. This is the case for the electrodes of Table 4. The aged suspension used for their preparation was more aggregated. The electrodes were thicker. This produced more ordered films. The difference in  $c_1$  of the different forms disappeared.

Why is  $c^*$  generally smaller for the enantiomers than for the racemic mixtures? In a recent report [64] we concluded that the presence of defects in the films giving access to the conductive substrate was the main factor in determining the electroactivity of these types of cations in clay modified electrodes. Since we conclude that adsorption of the enantiomers produced less aggregated, more disordered films, one would expect that  $c^*$  of the enantiomer would be larger. However, not all defects lead to electroactivity, only those that provide a pathway for the electron to the conductive substrate. More ordered films may have less defects, but a larger proportion of these could allow access to the substrate.

#### CONCLUSION

Spectroscopic measurements of the adsorption isotherm of  $\text{Ru}(\text{bpy})_3^{2+}$  show that only one equivalent of racemic cation was adsorbed, compared to two equivalents of the enantiomers. To explain these differences, it is proposed that adsorption of the different forms have different effects on the aggregation of the clays. The racemic pair adsorption model [32-36] was extended to take into account the layering of the clay particles. However, differences in the isotherms do not translate into differences in the cyclic voltammograms, since values of  $c^*/c_1$  were found to be different for the racemic mixture and the enantiomers.

While CME remain interesting types of modified electrodes, it seems clear that their electrochemical behavior can be quite complicated and a function of several factors. The effect of adsorption of the cation on the degree of aggregation of the clay that was found in these studies, and the fact that only a small fraction of adsorbed cations are electroactive, can lead to significant variation in observed electrochemical behavior with only small changes in experimental variables.

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