

## A Clay-modified Electrode with Stereoselectivity

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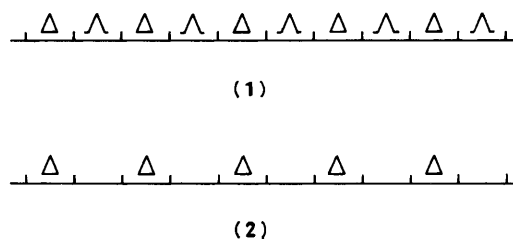
An SnO<sub>2</sub> glass electrode coated with a  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup>-montmorillonite clay film oxidized racemic Co(phen)<sub>3</sub><sup>2+</sup> (phen = 1,10-phenanthroline) at 30 °C to produce  $\Lambda$ -Co(phen)<sub>3</sub><sup>2+</sup> with 7% optical purity.

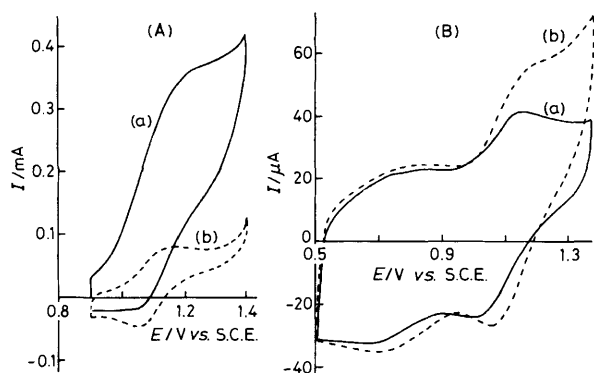
Recently it was reported that certain tris-chelated complexes were adsorbed by a clay, with a racemic pair being adsorbed as a single unit.<sup>1</sup> For example, racemic Fe(phen)<sub>3</sub><sup>2+</sup> (phen = 1,10-phenanthroline) covered the whole surface of a clay with an alternating sequence of the  $\Delta$ - and  $\Lambda$ -enantiomers, (1), whereas enantiomeric Fe(phen)<sub>3</sub><sup>2+</sup> covered only 50% of the surface because of the steric interference between the adjacent adsorbents.<sup>1</sup> These results led us to pursue the possibility that, if a chemical reaction took place on a clay modified by an optically active chelate (2), it might proceed stereoselectively to produce an optically active molecule. Such an effect was expected because an unoccupied site in (2) could exclusively accept the optical antipode of the primarily adsorbed molecule. In the present study, this selectivity was demonstrated by the electrolytic oxidation of racemic Co(phen)<sub>3</sub><sup>2+</sup> on an SnO<sub>2</sub> electrode coated with a  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup>-montmorillonite clay film.  $\Lambda$ -Co(phen)<sub>3</sub><sup>2+</sup> was produced in enantiomeric excess owing to stereoselective adsorption onto the clay film.

A clay-modified electrode was prepared according to the method of Ghosh and Bard.<sup>2</sup> An SnO<sub>2</sub>-coated glass plate (0.7

× 2 cm) was soaked in a solution of sodium montmorillonite (10 g l<sup>-1</sup>) and polyvinyl alcohol (2 g l<sup>-1</sup>), and subsequently dried to yield a film electrode.  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup> was incorporated into the clay by immersing the electrode in a 7 mM  $\Delta$ -Ru(phen)<sub>3</sub>Cl<sub>2</sub> solution overnight. The electrode was then washed with water several times until no  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup> dissolved from the electrode.

Figure 1(A) shows the cyclic voltammogram at 50 mV/s in 0.05 M Na<sub>2</sub>SO<sub>4</sub>. The initial current-voltage curve (a) changed gradually to the stationary curve (b) after ca. 20 scans. In the stationary state, the peaks at 1.18 and 1.08 V vs. the saturated





**Figure 1.** (A) Cyclic voltammograms at 50 mV/s in 0.05 M Na<sub>2</sub>SO<sub>4</sub> for  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup> incorporated into a clay film on SnO<sub>2</sub> electrodes. (a) initial scan, and (b) after ca. 20th scan. Electrode area 10 cm<sup>2</sup>. (B) Cyclic voltammograms at ca. 15th scan of 0.2 V/s. (a)  $6 \times 10^{-5}$  M  $\Delta$ -Ru(phen)<sub>3</sub>Cl<sub>2</sub> + 0.1 M Na<sub>2</sub>SO<sub>4</sub>. (b)  $6 \times 10^{-5}$  M  $\Lambda$ -Ru(phen)<sub>3</sub>Cl<sub>2</sub> + 0.1 M Na<sub>2</sub>SO<sub>4</sub>. Electrode area 3 cm<sup>2</sup>.

calomel electrode (S.C.E) were observed in anodic and cathodic sweeps, respectively. The  $E_{1/2}$  from these peak potentials was at 1.13 V; the formal redox potential of Ru(phen)<sub>3</sub><sup>2+</sup>/Ru(phen)<sub>3</sub><sup>3+</sup> in 1 M H<sub>2</sub>SO<sub>4</sub> was reported to be 1.02 V vs. S.C.E.<sup>3</sup> The difference of the peak potentials was 0.1 V. Therefore it was concluded that the  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup> adsorbed onto the clay was reversibly oxidized at the SnO<sub>2</sub> electrode.

When  $6 \times 10^{-5}$  M  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup> was added to the electrolyte solution, no significant change occurred in the cyclic voltammogram [Figure 1(B) curve a]; *i.e.*, the presence of excess of  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup> in the solution had no influence on the redox reaction at the clay film-SnO<sub>2</sub> electrode interface. In contrast, the voltammogram changed considerably when  $6 \times 10^{-5}$  M  $\Lambda$ -Ru(phen)<sub>3</sub><sup>2+</sup> was added to the solution [Figure 1(B) curve b]. The current increased by almost 1.5 times at  $E = 1.1$  V vs. S.C.E. in the anodic sweep, while the current changed little in the cathodic sweep. The observed effect of  $\Lambda$ -Ru(phen)<sub>3</sub><sup>2+</sup> was reversible; curve (b) reverted to curve (a) when the solution was replaced with a solution of  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup> again. The results suggested that  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup> was repelled from the  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup>-montmorillonite film, while  $\Lambda$ -Ru(phen)<sub>3</sub><sup>2+</sup> in the electrolytic

solution penetrated the clay film until the  $\Lambda$ -Ru(phen)<sub>3</sub><sup>2+</sup> was oxidized to  $\Lambda$ -Ru(phen)<sub>3</sub><sup>3+</sup> at the SnO<sub>2</sub> electrode. At present it is not clear why the production of  $\Lambda$ -Ru(phen)<sub>3</sub><sup>3+</sup> did not contribute to an increase in the current in the cathodic sweep; it is possible that the  $\Lambda$ -Ru(phen)<sub>3</sub><sup>3+</sup> produced is reduced to  $\Lambda$ -Ru(phen)<sub>3</sub><sup>2+</sup> homogeneously. Apart from this, the results confirm that a film of a clay-metal chelate adduct makes an SnO<sub>2</sub> electrode stereoselective towards a redox reaction of the same kind of metal chelate. Such stereoselectivity apparently arises from the stereoregular stacking of adsorbed molecules as in (1) and (2).

The above results show that in a racemic mixture electrolytic oxidation of selective  $\Lambda$ -Co(phen)<sub>3</sub><sup>2+</sup> occurred by penetrating the clay film stereoselectively to yield  $\Lambda$ -Co(phen)<sub>3</sub><sup>3+</sup> on the SnO<sub>2</sub> electrode. Co(phen)<sub>3</sub><sup>2+</sup> racemizes rapidly in water.<sup>4</sup> Since the resultant  $\Lambda$ -Co(phen)<sub>3</sub><sup>3+</sup> is inert to racemization, optical activity due to the stereoselective production of  $\Lambda$ -Co(phen)<sub>3</sub><sup>3+</sup> can be observed. An aqueous solution of 0.05 M Na<sub>2</sub>SO<sub>4</sub> and ca.  $1.4 \times 10^{-4}$  M racemic Co(phen)<sub>3</sub><sup>2+</sup> was electrolysed at 30 °C at an electrode potential of 1.3 V vs. S.C.E. The electrolysis ceased after 16 h when the current decreased from 75 to 4  $\mu$ A. The final solution was analysed by means of u.v. and c.d. spectra. The c.d. spectrum obtained was compared with the spectrum of a sample of  $\Lambda$ -Co(phen)<sub>3</sub><sup>3+</sup> which had been prepared independently.<sup>5</sup> The spectra show that Co(phen)<sub>3</sub><sup>2+</sup> was completely oxidized to Co(phen)<sub>3</sub><sup>3+</sup> with  $\Lambda$ -Co(phen)<sub>3</sub><sup>3+</sup> in 7% enantiomeric excess. Although the observed selectivity was much lower than expected, these results are the first example of a clay-optically active metal-chelate adduct film electrode inducing asymmetric electrode reactions.

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