# Δ-Ni(phen)$_3$$^{2+}$–Montmorillonite as a Template for Asymmetric Syntheses (phen = 1,10-Phenanthroline)

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Colloidal particles of Δ-Ni(phen)$_3$$^{2+}$–montmorillonite (phen = 1,10-phenanthroline) act as asymmetric templates in the reactions of (i) Co$^{2+}$ with 1-(2-pyridylazo)-2-naphthol to form an optically active Co$^{III}$ complex and (ii) the reduction of benzil with NaBH$_4$ to (*S,S*)-1,2-diphenylethane-1,2-diol.

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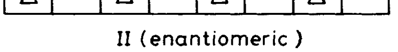
Recently it was reported that certain tris(chelated) complexes were adsorbed by colloidally dispersed sodium montmorillonite to different maximum amounts when added as the pure enantiomer or a racemic mixture.[1] For example, enantiomeric Fe(phen)$_3$$^{2+}$ was adsorbed to an amount within the cation-exchange capacity of the clay, whereas racemic Fe(phen)$_3$$^{2+}$ was adsorbed in a two-fold excess of this amount. It was concluded that racemic Fe(phen)$_3$$^{2+}$ covered the whole surface of a clay with an alternating sequence of the Δ- and Λ-enantiomers, while enantiomeric Fe(phen)$_3$$^{2+}$ covered only half of the surface owing to the steric interference between the chelates.

This finding prompted a study of the possibility that the vacant spaces around the enantiomeric chelates in state (II) might provide a site for stereoselective chemical reactions. This possibility was strengthened by the observation of the induction of optical activity in a molecule bound to Δ-Ni(phen)$_3$$^{2+}$–montmorillonite.

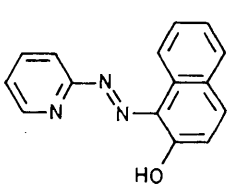
I (racemic)



II (enantiomeric)

Figure 1(a) gives the c.d. spectrum of a solution of colloidally dispersed Δ-Ni(phen)$_3$$^{2+}$–montmorillonite. The negative absorption below 350 nm was due to bound Δ-Ni(phen)$_3$$^{2+}$. When a neutral molecule, 1-(2-pyridylazo)-2-naphthol (Hpan), was added to the solution, a new c.d. peak appeared around 500 nm, Figure 1(b). Since Hpan is itself achiral and has an absorption peak at 475 nm, the observed c.d. peak was ascribed to Hpan molecules bound to Δ-Ni(phen)$_3$$^{2+}$–montmorillonite. The results implied that the bound molecules experienced an asymmetric field due to optically active Δ-Ni(phen)$_3$$^{2+}$. Encouraged by the above observation, the syntheses of two optically active compounds were investigated.

In the formation of the complex Co(pan)$_2$$^{+}$, Hpan (0.2 mg) in methanol (0.5 ml) was added to an aqueous solution (10 ml) containing Δ-Ni(phen)$_3$$^{2+}$–montmorillonite (120 mg; 10$^{-4}$ mol in terms of cation-exchange capacity);



Hpan

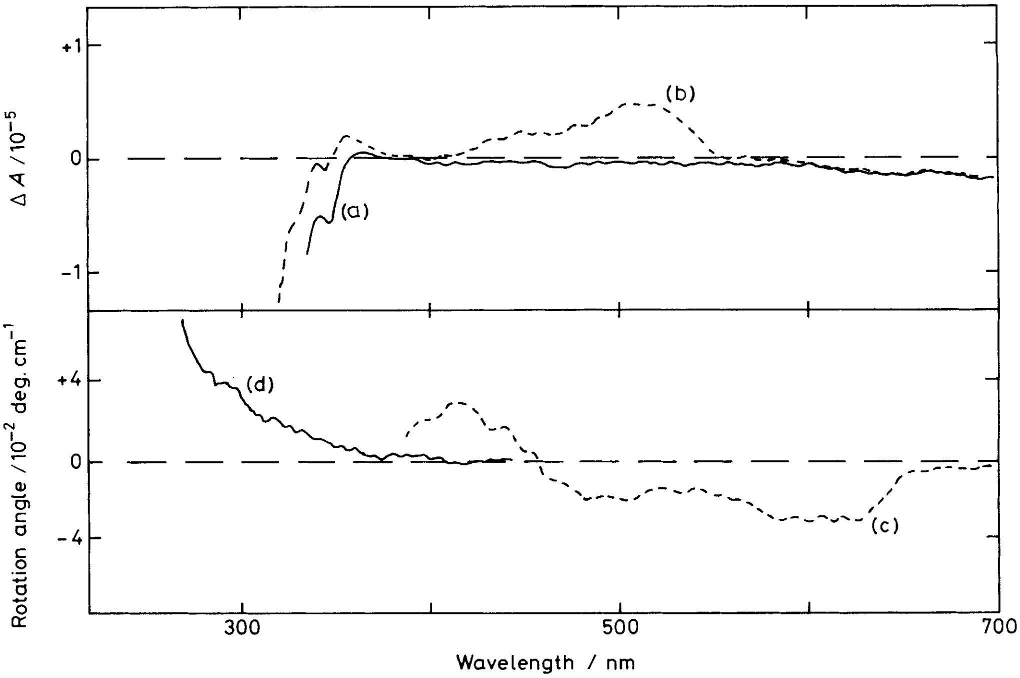


**Figure 1.** (Upper) (a) the c.d. spectrum of an aqueous solution of Δ-Ni(phen)$_3^{2+}$–montmorillonite (1.7 × $10^{-5}$ M in terms of cation-exchange capacity). The cell length was 10 cm. (b) The c.d. spectrum when Hpan ($10^{-5}$ M) was added to (a). (Lower) (c) The o.r.d. curve of the MeOH extract from the reaction of $Co^{2+}$ with Hpan in the presence of Δ-Ni(phen)$_3^{2+}$–montmorillonite. The curve coincided with that of $(-)_{600}$-Co(pan)$_2^+$ whose $[M]_{600}$ was previously determined to be 4.7 × $10^4$ (ref. 2). (d) The o.r.d. curve of the filtrate from the reduction of benzil with $NaBH_4$ in the presence of Δ-Ni(phen)$_3^{2+}$–montmorillonite. The curve coincided with that of an authentic sample of (*S*,*S*),1,2-diphenylethane-1,2-diol, whose $[M]_{300}$ value was determined to be 2800.

$CoCl_2 \cdot 6H_2O$ (0.1 mg) in water (0.5 ml) was added with stirring and the mixture changed from orange to green in 30 min. The mixture was filtered, the precipitate boiled in MeOH (50 ml; 40 °C; 30 min), and the mixture filtered. The filtrate contained $(-)_{600}$-Co(pan)$_2^+$ (3 × $10^{-7}$ mol; optical purity 30% from absorption and o.r.d. spectra). A second extraction of the precipitate with MeOH gave $(-)_{600}$-Co(pan)$_2^+$ ($10^{-7}$ mol; optical purity 50%). The o.r.d. spectrum is shown in Figure 1(c).

For the reduction of benzil, benzil (50 mg) in MeOH (20 ml) was added to an aqueous solution (20 ml) containing Δ-Ni(phen)$_3^{2+}$–montmorillonite (240 mg, 2 × $10^{-4}$ mol). The mixture was filtered and washed with water. About 10 mg of the benzil initially added was adsorbed by the clay. The precipitate was dispersed in water (50 ml) and $NaBH_4$ (200 mg) was added under $N_2$. The mixture turned slightly dark in 30 min and was filtered. The absorption spectrum of the filtrate coincided with that of 1,2-diphenylethane-1,2-diol. The o.r.d. spectrum indicated that the filtrate contained the (*S*,*S*)-isomer ($10^{-7}$ mol; optical purity >5%) [Figure 1(d)]. The exact value for the optical purity was not determined, since the ratio of (*RS*)- to *meso*-isomers was not known.

In both these examples, one of the enantiomers of the product was obtained preferentially owing to the interaction of the reactants with Δ-Ni(phen)$_3^{2+}$ on a clay. The results confirm the potential utility of a clay–optically active chelate adduct as a template for asymmetric syntheses.

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## References

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