Partial Resolution of Tris(acetylacetonato)ruthenium(III) on a Liquid Chromatography Column of Δ-Tris(1,10-phenanthroline)-nickel(II) Montmorillonite

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Summary Liquid chromatography on a Δ-tris(1,10-phenanthroline)nickel(II) montmorillonite column partially resolved tris(acetylacetonato)ruthenium(III), resulting in molecular rotations at 490 nm of −9200 and 6700 for the Λ- and Δ-isomers, respectively.

THE resolution of metal tris(β-diketonates) has been of great difficulty experimentally.[1–6] Since these chelates are molecular substances and contain no functional group, they do not undergo stoicheiometric combination with optically active resolving agents. As an alternative method, liquid column chromatography has been successful but is of relatively low efficiency; *e.g.*, the resolution was 10—20% for the first-eluted fraction of tris(acetylacetonato)cobalt(III).[2–6]

The present paper reports the first chromatographic application of a clay for the resolution of tris(acetylacetonato) ruthenium(III). The method is based on the recent finding that a bulky metal chelate like a metal tris(phenanthroline) complex stacks in a stereospecific manner when it is adsorbed on a colloidal clay.[7,8]

Δ-Tris(1,10-phenanthroline)nickel(II) montmorillonite [Δ-Ni(phen)$_3{}^{2+}\cdot 2M^-$] was prepared by adding the equivalent amount of Δ-[Ni(phen)$_3$]Cl$_2$ to a suspended solution of sodium montmorillonite. After centrifuging the solution, the clay–metal chelate complex was collected and washed with methanol. 1 g of the dried pink solid thus obtained was poured as a slurry in water into a glass tube. The whole column ($2\cdot5 \times 1\cdot0$ cm o.d.) was cooled at 2 °C to prevent racemization of the Δ-[Ni(phen)$_3$]$^{2+}$. It was ascertained that no light-absorbing species (340—700 nm) were eluted when water or methanol was allowed to flow through the column. The average flow rate was *ca.* 0·5 ml/min with a water-jet pump.

2 ml of aqueous Ru(acac)$_3$ ($1\cdot6 \times 10^{-6}$ mol) were placed on the column. No ruthenium chelate was separated on elution with pure water. When a 4 : 1 (v/v) water–methanol solvent was used, however, *ca.* 30% of Ru(acac)$_3$ was recovered in the first 20 ml of elution. The first-eluted fraction was concentrated to a 3 ml solution (solution A). The next 20 ml fraction contained 10% of the chelate. At the end of this step, the eluant contained less than 10^{-5} mol l^{-1} of Ru(acac)$_3$. Thereafter the rest of the chelate was recovered by eluting with 10 ml of methanol. The last eluted fraction was evaporated to dryness and dissolved in a 3 ml solution (solution B).

From the o.r.d. curves at 400—700 nm,[5] the solutions A and B contained excesses of Λ- and Δ-Ru(acac)$_3$ chelates, respectively, with molecular rotations of −9200 and +6700 at 490 nm, respectively. These values were comparable with those obtained in the first-eluted fraction by Fay *et al.* [−8000 for Λ-Ru(acac)$_3$].[5] The results are surprising when one compares the length of the present column (2·5 cm) with that of theirs (320 cm).

The above efficient resolution is due to the *enantiomeric* affinity of Δ-Ru(acac)$_3$ toward Δ-[Ni(phen)$_3$]$^{2+}\cdot 2M^-$. The tendency is in marked contrast with the previous observation that Λ-[Fe(phen)$_3$]$^{2+}$ is adsorbed *racemically* in the presence of Δ-[Ni(phen)$_3$]$^{2+}$ on a colloidal clay.[7,8] The difference in stereospecificity between these chelates may lie in the fact that [Fe(phen)$_3$]$^{2+}$ is adsorbed strongly on a free clay surface, while Ru(acac)$_3$ is not adsorbed unless the surface is modified by [Ni(phen)$_3$]$^{2+}$. In other words, the recognition of chirality by the column is dependent on which part of the column a metal chelate to be resolved is bound. Thus, a simple molecular stacking model has led us to the following conclusions. If [Fe(phen)$_3$]$^{2+}$ is adsorbed *adjacent to* [Ni(phen)$_3$]$^{2+}$, the racemic pairing is preferred to the enantiomeric one, while, if Ru(acac)$_3$ is adsorbed *over* [Ni(phen)$_3$]$^{2+}$, the preference is reversed.†

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† The C_3 axes of [Fe(phen)$_3$]$^{2+}$, [Ni(phen)$_3$]$^{2+}$, and Ru(acac)$_3$ were assumed to be vertical to the clay surface. In the case of [Fe(phen)$_3$]$^{2+}$, this was verified by electric dichroism measurements. Details will be published elsewhere.

[1] F. P. Dwyer and E. C. Gyarfas, *Nature*, 1951, **168**, 29.
[2] T. Moeller and E. Guylas, *J. Inorg. Nucl. Chem.*, 1958, **5**, 245.
[3] V. F. Doron and S. Kirschner, *Inorg. Chem.*, 1962, **1**, 539.
[4] J. P. Collman, R. P. Blair, R. L. Marshall, and L. Slade, *Inorg. Chem.*, 1963, **2**, 576.
[5] R. C. Fay, A. Y. Girgis, and U. Klabunde, *J. Am. Chem. Soc.*, 1970, **92**, 7056.
[6] M. Yamamoto, E. Iwamoto, A. Kozawa, K. Takemoto, Y. Yamamoto, and A. Tatekata, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 71.
[7] A. Yamagishi and M. Soma, *J. Chem. Soc., Chem. Commun.*, 1981, 539.
[8] A. Yamagishi and M. Soma, *J. Am. Chem. Soc.*, 1981, **103**, 4640.