CHEMISTRY LETTERS, pp. 85-88, 1982.

CHROMATOGRAPHIC RESOLUTION OF TRIS(ACETYLACETONATO)-COBALT(III) ON A Δ-TRIS(1,10-PHENANTHROLINE)NICKEL(II) MONTMORILLONITE COLUMN

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Tris(acetylacetonato)Co(III) was partially resolved on a 2.5 × 1.5 cm o.d. chromatographic column of Δ-tris(1,10-phenanthroline)Ni(II) montmorillonite at 2°C. The percentage resolution of Λ-tris(acetylacetonato)Co(III) was attained to be 36% for the first eluted fraction.

Although a clay itself has no asymmetric character at its binding site, there exists a rigorous steric regulation for the stacking of a bulky metal chelate over the clay surface. For example, tris(1,10-phenathroline)iron(II) ion is always adsorbed as a racemic pair on a colloidal clay.[1,2] As a result, the optical purity of a partially resolved solution improves by adding this clay, when the excess racemic mixture is eliminated as a clay-metal chelate adduct.[1,2] These facts have motivated us to try the chromatographic resolution of a metal chelate, using the column of a clay-metal chelate adduct. We report here that Δ-tris(1,10-phenanthroline)nickel(II) montmorillonite (Δ-$[Ni(phen)_3]^{2+}\cdot 2M^-$) has demonstrated the outstanding capability to resolve tris(acetylacetonato)cobalt(III)($[Co(acac)_3]$) in the liquid column chromatography. The separation of the complex has been a serious experimental difficulty, because it is a molecular complex and does not interact with any resolving agent.

7.0 g of sodium montmorillonite (Na^+M^-)(Kunipia-G, Kunimine Co. Ind., Japan) was dispersed in 400 ml of distilled water. The solution contained 8.0×10^{-3} equivalent of cation-exchange site.[3] 50 ml of aqueous 4.0×10^{-3} mole Δ-$[Ni(phen)_3]Cl_2$ was added to the clay solution under stirring. After centrifuging the solution, the clay-metal chelate adduct was collected and washed with methanol. The dried pinkish solid was ground into fine powders (∿9g). A slurry of 1.0 g of the solid in water was poured into a glass tubing to form a chromatographic column of 2.5 × 1.5 cm od. In order to prevent the racemization of Δ-$[Ni(phen)_3]^{2+}$, the column was cooled at 2°C.

5 ml of 2.4×10^{-3} M $[Co(acac)_3]$ was placed on the column and eluted with distilled water at a flow rate of 0.2 - 0.3 ml/min. An eluate was collected at every 3 ml and analyzed from the electronic and optical rotatory dispersion (ORD) spectra. The concentration of $[Co(acac)_3]$ was determined by using the molar extinction coefficient of 150 at 600 nm.

The water eluate gave the electronic spectrum which was identical with that of $[Co(acac)_3]$ in 340 - 700 nm.[4,6] About 60 ml of water was flowed until the concentration of eluted $[Co(acac)_3]$ became lower than the detection limit (2×10^{-5}M). Thereafter the rest of the bound metal chelate was eluted by methanol. The methanol eluate was collected to a single solution (∿30 ml).

Figure 1 shows the plots of the concentration of $[Co(acac)_3]$ and the molecular rotation at 530 nm, [M], against the elution volume. The vertical axis was also scaled in terms of the percentage resolution defined by $[M]/[M]_o$ with $[M]_o = -2.9 \times 10^4$ for Λ-$[Co(acac)_3]$.[4)] The last plot in the figure was for the methanol eluate, using $[M]_o = +2.9 \times 10^4$ for Δ-$[Co(acac)_3]$.[4)]

Most strikingly the water eluate always contained Λ-$[Co(acac)_3]$ as excess enantiomer. A greater part of Δ-$[Co(acac)_3]$ was bound with the clay column so strongly that it was recovered only by methanol solvent. Such a distinct separation has never been achieved, when other chromatographic columns were used for this kind of metal complexes.[4-7)] Accordingly the percentage resolution attained a value by far better than the reported one; 36% for Λ-$[Co(acac)_3]$ which was two times better than the best one reported (19.6%).[7,8)] The results are even more surprising, when one compares the length of the present column (2.5 cm) with the reported ones (60 - 200 cm).

The water eluate was collected to a single solution and was passed through the same column again. The resultant eluate (∿10 ml) thus obtained contained 86% of Λ-$[Co(acac)_3]$ out of the total concentration of 4.0×10^{-4} M (72% resolution). Thus the column was proved to be effective for repeated separations.

The present enantiometric affinity of $[Co(acac)_3]$ toward Δ-$[Ni(phen)_3]^{2+}\cdot 2M^-$ is completely contrary to the previous observation, in which Λ-$[Fe(phen)_3]^{2+}$ or Λ-$[Fe(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridine) is adsorbed preferentially with Δ-$[Ni(phen)_3]^{2+}$ on a colloidal clay.[1,2)] From the transient electric dichroism measurements, $[Fe(phen)_3]^{2+}$ orients its C_3 axis perpendicular to the clay surface.[9)] When this type of chelate covers a clay surface in such an lignment, the racemic body leads to the two-fold denser degree of stacking than the single enantiomer. The adsorption as a racemic pair is therefore ascribed to the preferable stacking of Λ-$[Fe(phen)_3]^{2+}$ (or Λ-$[Fe(bipy)_3]^{2+}$) by the side of adsorbed Δ-$[Ni(phen)_3]^{2+}$.

The reasons for the preferential adsorption of the one enantiomer in the present system were investigated by adding colloidal Na^+M^+ to a solution of $[Co(acac)_3]$ and Δ-$[Ni(phen)_3](ClO_4)_2$. As is given in Table 1, the following points are concluded; (i) No $[Co(acac)_3]$ was adsorbed on a clay in the absence of $[Ni(phen)_3]^{2+}$. (ii) Λ-$[Co(acac)_3]$ was adsorbed preferentially, when the ratio of $[Ni(phen)_3]^{2+}$ to $[Na^+M^-]$ was small. (iii) Δ-$[Co(acac)_3]$ was adsorbed preferentially, when the ratio was large. These results imply that, when the whole cation-exchange sites of M^- are preoccupied by Δ-$[Ni(phen)_3]^{2+}$, $[Co(acac)_3]$ does not lie on a montmorillonite surface directly, but it is located over the adsorbed layer of nickel chelates. If $[Co(acac)_3]$ takes such a position with its C_3 axis perpendicular to the surface, the Δ-isomer is more stably stacked with Δ-$[Ni(phen)_3]^{2+}$ than the Λ-isomer. This explains why Δ-$[Co(acac)_3]$ is bound with the present column more strongly than Λ-$[Co(acac)_3]$.

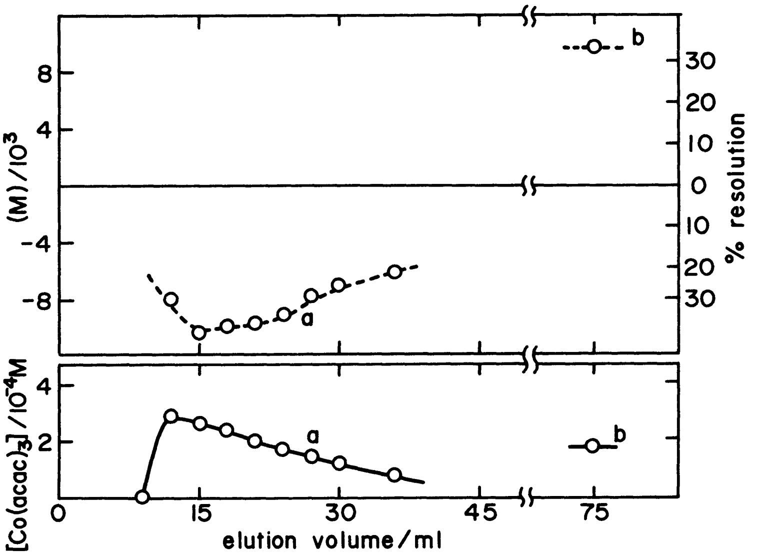

Figure 1. The elution curve of [Co(acac)$_3$]. The curve a is the elution curve for water solvent. The plot b is the eluate for methanol solvent. The solid curve (lower) denotes the concentration of [Co(acac)$_3$] in an eluate, and the dotted curve (upper) the molecular rotation at 530 nm.

A clay column is inexpensive and easy to prepare. Moreover, the present method has a vast versatility in the sense that various kinds of metal complexes are able to be adsorbed at a cation-exchange site. For example, if asymmetric ligands are introduced in the pre-adsorbed metal chelates, the resultant column may be able to resolve not only organo-metallic compounds as described above but also small organic compounds.

TABLE 1.

Adsorption of $[Co(acac)_3]$ on sodium montmorillonite (Na^+M^-)
in the presence of Δ-$[Ni(phen)_3](ClO_4)_2$

Run	Δ-$[Ni(phen)_3]^{2+}$/ 10^{-4}M[a)]	adsorbed $Co(acac)_3$/ 10^{-4}M[b)]	excessive isomer in the solvent/10^{-5}M[c)]
1	0.0	less than 0.2	none
2	1.4	0.5	0.4 (Δ)
3	2.9	0.9	0.8 (Δ)
4	4.0	2.1	1.5 (Δ)
5	5.8	2.5	8.0 (Λ)

a) The initial amount of Δ-$[Ni(phen)_3](ClO_4)_2$, which was present in a solution of 1.42×10^{-3}M $[Co(acac)_3]$ and 1.1×10^{-3}M Na^+M^-.

b) The adsorbed amount of $[Co(acac)_3]$ on a clay, which was obtained by centriguging the solution.

c) The excessive optical isomer of $[Co(acac)_3]$, which was present in a supernatant solution.

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8) Under the experimental conditions where the column kept below 2°C, similar resolution efficiencies were obtained on the column made from a different lot of Na^+M^- and for repeated use of the same column.
9) Measurements were performed with the instrument described in A. Yamagishi, Biopolymers, 20, 201 (1981).

(Received November 5, 1981)