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CLAY COLUMN CHROMATOGRAPHY FOR OPTICAL RESOLUTION: PARTIAL RESOLUTION OF TRIS(ACETYLACETONATO)METAL(III) ON A Δ -TRIS(1,10-PHENANTHROLINE)RUTHENIUM(II) MONTMORILLONITE COLUMN

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SUMMARY

Racemic mixtures of tris(acetylacetonato)metal(III) [M(III)(acac)₃, M = Co, Cr and Rh] were partially resolved on a 0.6 × 1.2 cm O.D. liquid chromatographic column of Δ -tris(1,10-phenanthroline)ruthenium(II) montmorillonite. For Co(acac)₃, the maximum resolutions were 61 and 70% for Δ - and Δ -enantiomers, respectively. The efficiency of the column was maintained when it was subjected to repeated runs and storage for long periods at room temperature.

INTRODUCTION

Recently, we reported that clay is a good column material for resolving racemates of metal complexes^{1–3}. The work was initiated by the finding that a racemate of a tris(chelated) complex was adsorbed on clay twice as much as a corresponding enantiomer in aqueous solution⁴. The results indicated that a surface saturated with a given enantiomer could further accept the binding of its optical antipode. The Δ - and Δ -isomers were likely to be stacked in an alternative manner inside the interlayer space of a clay. As a consequence of these stereoregular stackings, a clay modified by an optically active chelate may be able to recognize the absolute configuration of an approaching molecule in terms of preference for stacking partner⁵.

The above expectation was realized by liquid chromatography on a sodium montmorillonite (Na⁺M⁻) column whose cation-exchange sites were completely replaced with Δ -tris(1,10-phenanthroline)nickel(II) (Δ -Ni(phen)₃²⁺)^{1–3}. The column [denoted by Δ -Ni(phen)₃²⁺ · 2M⁻] attained a 90% one-pass resolution with Co(acac)₃ at 2°C³. The results were surprising when they were compared with the performances on other known columns (e.g., 15% resolution on a 480 × 5 cm I.D. *d*-lactose hydrate column⁶).

In spite of its potential, however, Δ -Ni(phen)₃²⁺ · 2M⁻ has the disadvantage as

a coupling material with clay from the practical point of view that the column gradually loses its resolving efficiency when it is used at room temperature. This deterioration is caused by the racemization of adsorbed Δ -Ni(phen) $_3^{3+}$. In water, for example, the chelate racemizes with a half-life of 34 h at 25°C⁷. In order to overcome this difficulty, the cation-exchange sites in a clay should be occupied by an optically active chelate that is free from racemization at ambient temperature. In this work, three such chelates were used as pre-adsorbates: tris(ethylenediamine)cobalt(III) [Co(en) $_3^{3+}$], Co(phen) $_3^{3+}$ and Ru(phen) $_3^{2+}$. One of the results with Ru(phen) $_3^{2+}$ is particularly noteworthy: a column modified by optically active Ru(phen) $_3^{2+}$ not only resolved racemates of metal complexes with the same efficiency as Δ -Ni(phen) $_3^{2+} \cdot 2M^-$, but also maintained its resolving power on repeated use and with long periods of storage at room temperature. Thus, the applicability of clay columns to a wide range of metal complexes was increased.

EXPERIMENTAL

Δ -Co(en) $_3$ Cl $_3$ and Δ -Co(phen) $_3$ (ClO $_4$) $_3$ were prepared according to the literature⁸. Ru(phen) $_3$ Cl $_2$ was not obtained in a high yield when it was synthesized by the reported method⁸, so RuCl $_3 \cdot xH_2O$ (0.5 g) and phen $\cdot H_2O$ (5 g) were heated at 180–200°C for 10 h, giving Ru(phen) $_3$ Cl $_2$ in 70% yield. Purification and resolution of Δ -Ru(phen) $_3$ bis(antimonyl *d*-tartrate) were carried out as described in the literature⁹. Co(acac) $_3$, Cr(acac) $_3$ and Rh(acac) $_3$ were obtained in the reported manner⁸.

A stoichiometric amount of each metal complex corresponding to the cation-exchange capacity of Na $^+M^-$ (1.12 mequiv./g)¹⁰ was added to a solution of colloidal dispersed sodium montmorillonite (Na $^+M^-$, Kunipia-G; Kunimine Industry Co., Tokyo, Japan). The mixture was stirred for several hours until no solid added chelate was observed. After centrifuging the mixture, the supernatant was decanted. The precipitate was washed with methanol and dried under vacuum. During the above procedures, both Δ -Co(en) $_3^{3+}$ and Δ -Co(phen) $_3^{3+}$ were adsorbed quantitatively by the colloidal clay. The final products were denoted by Δ -Co(en) $_3^{3+} \cdot 3M^-$ and Δ -Co(phen) $_3^{3+} \cdot 3M^-$, respectively. With Δ -Ru(phen) $_3^{2+}$, 25% of the chelate loaded was not adsorbed by the clay, remaining in the supernatant solution. Accordingly, the final product was denoted by Δ -Ru(phen) $_3^{2+} \cdot 2.65M^-$. The residual cation-exchange sites might be occupied by Na $^+$ ions.

Tris(acetylacetonato)metal(III) chelate was chromatographed on a column packed with the material described above. The concentration of the chelate recovered in the eluate was determined with a Hitachi EPS-3T spectrophotometer. The optical rotation of the eluate was measured with a JEOL Model ORD/UV-5 optical rotatory dispersion spectrometer. The subsequent procedures were carried out at room temperature (15–20°C).

RESULTS

An aqueous suspension of 0.4 g of Δ -Co(en) $_3^{3+} \cdot 3M^-$ was used to prepare a 1.8 \times 1.0 cm O.D. column whose interstitial volume was 0.7 ml in water. A 2-ml volume of $2.0 \cdot 10^{-3}$ M Co(acac) $_3$ solution was placed on the column, and when water was passed through at a flow-rate of 0.03 ml min $^{-1}$, all of cobalt chelate was recovered

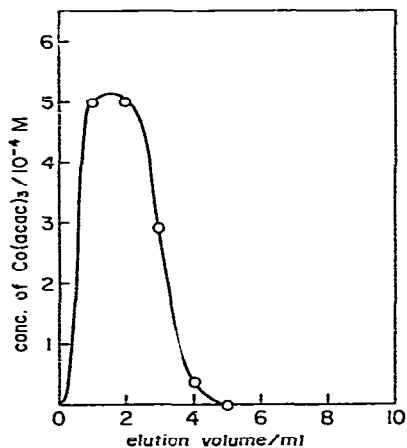


Fig. 1. Elution curve of $\text{Co}(\text{acac})_3$ (2 ml of $8 \cdot 10^{-4} M$ solution on a 1.5×1.2 cm O.D. column of $\Delta\text{-Co}(\text{phen})_3^{3+}$ montmorillonite. Eluent: water.

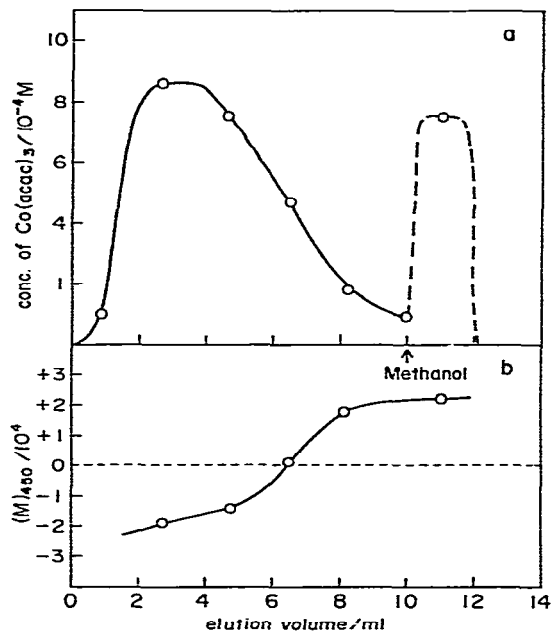


Fig. 2. (a) Elution curve of $\text{Co}(\text{acac})_3$ (2 ml of $4 \cdot 10^{-3} M$ solution) on a 0.6×1.2 cm O.D. column of $\Delta\text{-Ru}(\text{phen})_3^{2+}$ montmorillonite. Eluent: water until the elution volume attained 10 ml, then methanol. (b) Molecular rotation of each eluate at 450 nm plotted against elution volume.

within an elution volume of $V = 3$ ml. No optical rotation was detected in the eluate. As $\text{Co}(\text{acac})_3$ was eluted almost within the sum of the interstitial volume and the volume initially used ($0.7 + 2.0 = 2.7$ ml), the chelate showed no affinity towards the column. Accordingly, $\text{Co}(\text{acac})_3$ was not resolved.

A 0.5-g amount of $\Delta\text{-Co}(\text{phen})_3^{3+} \cdot 3\text{M}^-$ formed a 1.5×1.2 cm O.D. column whose interstitial volume was 0.5 ml. A 2-ml volume of $8 \cdot 10^{-4} M$ $\text{Co}(\text{acac})_3$ solution was placed on the column. When water was passed through at a flow-rate of 0.5 ml min^{-1} , the cobalt chelate was eluted as shown in Fig. 1. About 30% of the chelate still remained on the column when the elution volume attained the sum of the interstitial volume and the volume initially used ($0.5 + 2.0 = 2.5$ ml). This indicated that the chelate showed a slight affinity towards the column. No optical rotation was detected in the eluates, however. Thus both Δ - and Δ -isomers of $\text{Co}(\text{acac})_3$ were bound to the column with equal strength.

A 0.25-g amount of $\Delta\text{-Ru}(\text{phen})_3^{2+} \cdot 2.65\text{M}^-$ formed a 0.6×1.2 cm O.D. column whose interstitial volume was less than 0.2 ml. A 2-ml volume of $4.0 \cdot 10^{-3} M$ $\text{Co}(\text{acac})_3$ solution was placed on the column. When water was passed through at a flow-rate of 0.3 ml min^{-1} , the cobalt chelate was eluted as shown in Fig. 2a. The concentration of $\text{Co}(\text{acac})_3$ was less than $1 \cdot 10^{-4} M$ at an elution volume of 10 ml, at which stage about 25% of the loaded chelate was still bound to the column. The remaining chelate was recovered by elution with 2 ml of methanol. The molecular

rotation (M) of each effluent at 450 nm was plotted against the elution volume (Fig. 2b). Based on the assignment by Von Dreele and Fay¹¹, the positive and negative (M)₄₅₀ corresponded to Δ - and Λ -enantiomers as excess isomer, respectively. Thus, Δ -Co(acac)₃ was bound to the column more strongly than Λ -Co(acac)₃. As the present column was modified by Λ -Ru(phen)₃²⁺, Co(acac)₃ exhibited racemic affinity towards the column. The maximum resolutions were 61 and 70% for Λ - and Δ -Co(acac)₃, respectively, when (M)₄₅₀ for the pure Λ - and Δ -isomers were taken to be $-3.1 \cdot 10^4$ and $+3.1 \cdot 10^4$, respectively⁷.

The same procedures were repeated to test the durability of the column at room temperature. The maximum resolutions for the Δ -isomer were 80, 70 and 75% at 1, 2 and 33 days, respectively, after the column was prepared. The results showed that the column efficiency did not decrease at ambient temperature over long periods, as expected.

A 2-ml volume of $3.0 \cdot 10^{-3}$ M Cr(acac)₃ in methanol-water (1:3, v/v) was placed on the same Λ -Ru(phen)₃²⁺ - 2.65M⁻ column. When methanol-water (1:3, v/v) was passed through, 30% of the chromium chelate was recovered within an elution volume of 4 ml. The remainder of the chelate was so strongly bound to the column that it was not recovered with organic solvents such as methanol, ethanol, chloroform and their mixtures. The optical rotatory dispersion curve of the recovered chelate was identical with that of Δ -Cr(acac)₃¹². The molecular rotation of the Δ -isomer was -2100 at 560 nm. As Λ -Cr(acac)₃ still remained on the column, it was concluded that Cr(acac)₃ had enantiomeric affinity towards the column.

On the same column was placed 2 ml of $3 \cdot 10^{-3}$ M Rh(acac)₃ in methanol-water (1:2, v/v). When the same solvent as above was passed through the column, the chelate was eluted as shown in Fig. 3a. At an elution volume of 15 ml, the concentration of Rh(acac)₃ became lower than $1 \cdot 10^{-4}$ M. About 25% of the loaded chelate was still bound to the column. The residual chelate was recovered within an elution volume of 20 ml when pure methanol was used. The molecular rotation at 400 nm was plotted against the elution volume as shown in Fig. 3b. Mason *et al.*¹³ assigned the

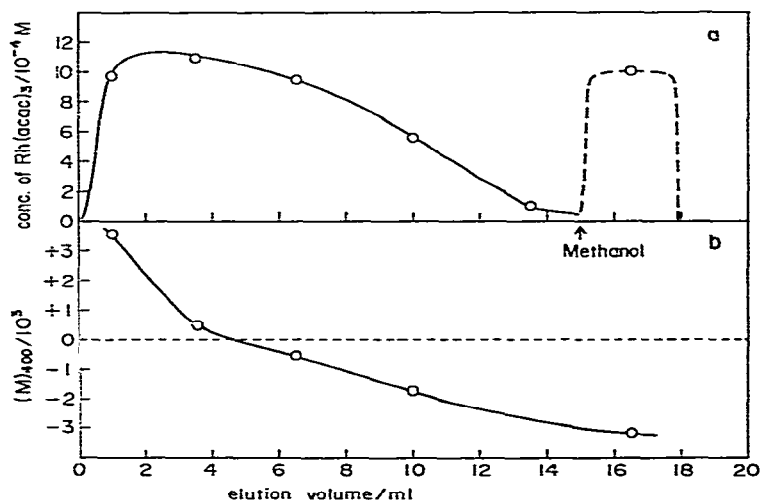


Fig. 3. (a) Elution curve of Rh(acac)₃ [2 ml of a $3 \cdot 10^{-3}$ M solution in methanol-water (1:2, v/v)] on the same column as in Fig. 2. Eluent: methanol-water (1:2, v/v) until the elution volume attained 15 ml, then methanol. (b) Molecular rotation of each eluate at 400 nm plotted against elution volume.

enantiomers with positive and negative signs of $(M)_{400}$ as the *A*- and *A*-isomer, respectively. Thus, this column also shows enantiomeric affinity towards $\text{Rh}(\text{acac})_3$. The maximum $(M)_{400}$ for these isomers were +3500 and -3100, respectively.

DISCUSSION

Of the three columns investigated, only $\text{Ru}(\text{phen})_3^{2+} \cdot 2.65\text{M}^-$ was able to resolve $\text{M}(\text{acac})_3$ racemates. $\text{Ru}(\text{phen})_3^{2+}$ has the same charge and the same three phenanthroline ligands as $\text{Ni}(\text{phen})_3^{2+}$, but the ionic radius of Ru^{2+} is about 0.25 Å larger than that of Ni^{2+} (0.68 Å) [estimated from structural data for $\text{Ru}(\text{C}_5\text{H}_5)_2$ in ref. 14]. A $\text{Ru}(\text{phen})_3^{2+} \cdot 2.65\text{M}^-$ column showed an efficiency in resolving $\text{Co}(\text{acac})_3$ similar to that of an $\text{Ni}(\text{phen})_3^{2+} \cdot 2\text{M}^-$ column. There are, however, two main differences between these two columns. (i) The $\text{Ru}(\text{II})$ column maintains its resolving power at room temperature for at least 1 month, whereas the $\text{Ni}(\text{II})$ column retained its efficiency only below 2°C. Apparently this difference arises from the fact that $\text{Ru}(\text{phen})_3^{2+}$ is a substitution-inert complex, whereas $\text{Ni}(\text{phen})_3^{2+}$ gradually racemizes at room temperature. (ii) The optical isomer of $\text{Co}(\text{acac})_3$ showing the stronger affinity towards the $\text{Ru}(\text{II})$ column has the opposite configuration to pre-adsorbed $\text{Ru}(\text{phen})_3^{2+}$ (racemic adsorption), whereas the isomer with the stronger affinity towards the $\text{Ni}(\text{II})$ column has the same configuration as pre-adsorbed $\text{Ni}(\text{phen})_3^{2+}$ (enantiomeric adsorption)². According to previous work³, the affinity of tris(acetylacetonato) $\text{M}(\text{III})$ towards a tris(phenanthroline) $\text{M}(\text{II})$ column is caused by the dispersive force between the CH_3 groups in acac and the phenanthroline ligands. To achieve the closest approach of these two groups, there are two different types of stacking of $\text{M}(\text{III})(\text{acac})_3$ with $\text{M}(\text{II})(\text{phen})_3^{2+}$. At one binding site, an adsorbed $\text{M}(\text{III})(\text{acac})_3$ and an $\text{M}(\text{II})(\text{phen})_3^{2+}$ sit side by side with their C_3 axes parallel (Fig. 4a). In this instance these two stacking chelates should take opposite configurations (racemic adsorption). At the other binding site an adsorbed $\text{M}(\text{III})(\text{acac})_3$ is placed over the head of $\text{M}(\text{II})(\text{phen})_3^{2+}$ sharing a common C_3 axis (Fig. 4b). In this instance, these two chelates should have the same configuration (enantiomeric adsorption). It is presumed that the above two sites are competitive for binding $\text{M}(\text{III})(\text{acac})_3$ in both the $\text{Ni}(\text{II})$ and $\text{Ru}(\text{II})$ columns.

Based on the present chromatographic data, the racemic adsorption site (Fig. 4a) predominates in binding $\text{Co}(\text{acac})_3$ on the $\text{Ru}(\text{phen})_3^{2+} \cdot 2.65\text{M}^-$ column, whereas the situations are reversed in binding $\text{Cr}(\text{acac})_3$ and $\text{Rh}(\text{acac})_3$. The results are contrasted with the performances of an $\text{Ni}(\text{phen})_3^{2+} \cdot 2\text{M}^-$ column, on which the enantiomeric adsorption site (Fig. 4b) predominates in binding each of $\text{Co}(\text{acac})_3$, $\text{Cr}(\text{acac})_3$ and $\text{Rh}(\text{acac})_3$ (refs. 1 and 2). The structural differences between $\text{Ru}(\text{phen})_3^{2+}$ and $\text{Ni}(\text{phen})_3^{2+}$ are not responsible for these discrepancies as long as chirality recognition is realized by the weak intermolecular forces as stated above (Fig. 4a and b). Instead, it may be explained by the fact that a proportion of the cation-exchange sites (ca. 25%) remain unoccupied by $\text{Ru}(\text{phen})_3^{2+}$ in the $\text{Ru}(\text{II})$ column, whereas the sites are completely occupied by $\text{Ni}(\text{phen})_3^{2+}$ in the $\text{Ni}(\text{II})$ column. Thus, it is likely that the binding of $\text{M}(\text{III})(\text{acac})_3$ at the racemic site is more favoured in the $\text{Ru}(\text{II})$ column than in the $\text{Ni}(\text{II})$ column. This is in accord with the results of the previous batch experiments in which $\text{Co}(\text{acac})_3$ was adsorbed racemically when a proportion of the cation-exchange sites of Na^+M^- were unoccupied by $\text{Ni}(\text{phen})_3^{2+}$ $\{[\text{Ni}(\text{phen})_3^{2+}]/[\text{Na}^+\text{M}^-] < 0.5\}$. On the other hand, $\text{Co}(\text{acac})_3$ is adsorbed enantiomerically when a large proportion of cation-exchange sites were occupied by $\text{Ni}(\text{phen})_3^{2+}$ $\{[\text{Ni}(\text{phen})_3^{2+}]/[\text{Na}^+\text{M}^-] > 0.5\}$. Hence the chirality recog-

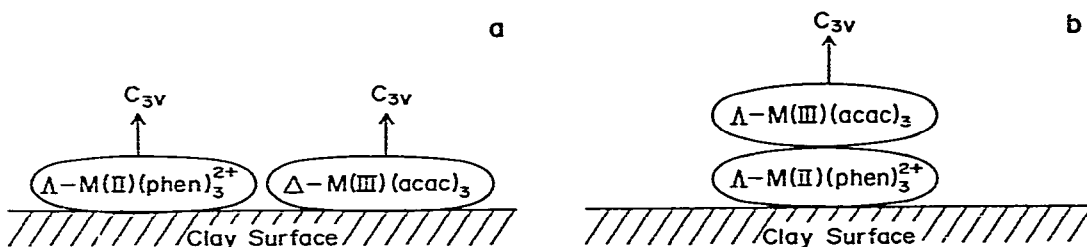


Fig. 4. Schematic representations of two types of binding of M(III)(acac)_3 with an $\text{M(II)(phen)}_3^{2+}$ montmorillonite column. (a) Racemic adsorption in which M(III)(acac)_3 and $\text{M(II)(phen)}_3^{2+}$ sit side by side. The paired chelates should have opposite configurations. (b) Enantiomeric adsorption in which M(III)(acac)_3 is located over the head of pre-adsorbed $\text{M(II)(phen)}_3^{2+}$. The paired chelates should have the same configuration.

nition for the binding of Co(acac)_3 depends on the degree of modification by a pre-adsorbed molecule. As for Cr(acac)_3 and Rh(acac)_3 , these chelates always prefer the enantiomeric site, whether there are vacant cation-exchange sites or not. The reasons for this are not clear at present.

On the Ru(II) column, Rh(acac)_3 was resolved at least partially, but the Ni(II) column hardly resolved it, although a very small optical rotation was detected. In this respect, the Ru(II) column was superior to the Ni(II) column. The $(M)_{400}$ attained ($+3500$ and -3100 for Δ - and Λ -isomers, respectively) was of a magnitude comparable to those obtained on a 480×5 cm I.D. d -lactose hydrate column⁶. The results are impressive when one considers the length of the column (0.6 cm).

CONCLUSIONS

On a 0.6×1.2 cm O.D. column of sodium montmorillonite 75% of whose cation-exchange sites were replaced with Δ -tris(1,10-phenanthroline)ruthenium(II) tris(acetylacetonato) complexes of cobalt(III), chromium(III) and rhodium(III) were partially resolved with maximum molecular rotations of $(M)_{400} = +22,000$, $(M)_{560} = -2100$ and $(M)_{400} = +3500$, respectively, for the Δ -isomers. The efficiency exhibited by the column was better than that of a 480×5 cm I.D. column of d -lactose hydrate reported in the literature.

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