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COMPLETE CHROMATOGRAPHIC RESOLUTION OF TRIS(ACETYLACETONATO)-COBALT(III) AND CHROMIUM(III) ON AN OPTICALLY ACTIVE POLY(TRIPHENYLMETHYL METHACRYLATE) COLUMN[1)]

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Tris(acetylacetonato)Co(III) and Cr(III) were completely resolved by HPLC on a (+)-poly(triphenylmethyl methacrylate) column. Optical data of pure enantiomers were obtained and the structure of the polymer was discussed on the basis of the results of the resolution.

Resolution of electrically neutral complexes such as trisacetylacetonates of trivalent metals is difficult because of the lack of functionalities for resolution.[2)] Liquid chromatography on chiral materials is one of practical methods for the resolution of such complexes.[2-6)] However, only partial resolution has so far been attained by this method. We found recently that optically active poly(triphenylmethyl methacrylate) (PTrMA),[7,8)] particularly that coated on silica gel,[9)] is a useful packing material for the chromatographic resolution of a wide variety of organic compounds. We report here the complete resolution of [Co(acac)$_3$] and [Cr(acac)$_3$] by high-performance liquid chromatography (HPLC) on the chiral polymer and the optical data of the pure enantiomers obtained. The results of the resolution afforded valuable information on the structure of (+)-PTrMA.

The preparations of (+)-PTrMA[10)] and the polymer-coated silica gel[9)] for HPLC have been reported previously. The chromatography was performed on a JASCO TRI ROTAR-II equipped with a UV-100-III detector at 15°C. Theoretical plates number of a column (25cm × 0.46cm(id)) for acetone was ∿5000 when methanol was used as an eluent. The optical rotation and CD spectrum were measured with a 5-cm cell on a JASCO DIP-181 polarimeter and with a 1-cm cell on a JASCO CD apparatus J40,

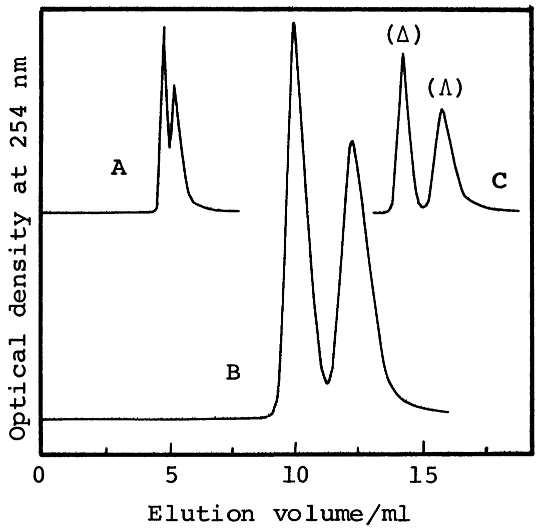

Fig. 1. Chromatograms of resolution of $[Cr(acac)_3]$ on (+)-PTrMA column.

Column: 25 × 0.46 (id) cm (A, B)
75 × 0.46 (id) cm (C)
Eluent: methanol (A, C)
methanol-water (80/20) (B)
Flow rate: 0.5 ml/min
Temperature: 15°C

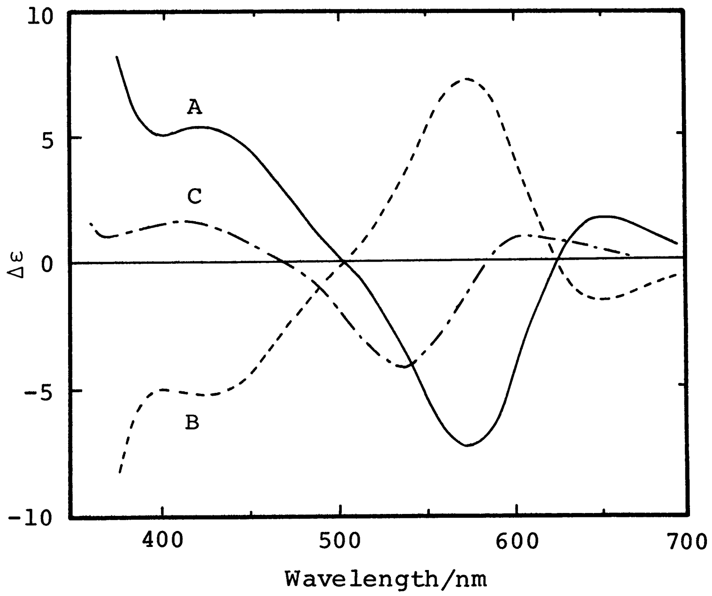

Fig. 2. CD spectra of optically pure complexes in benzene.

A: 1st-eluted Δ-isomer of $[Co(acac)_3]$
B: 2nd-eluted Λ-isomer of $[Co(acac)_3]$
C: 1st-eluted Δ-isomer of $[Cr(acac)_3]$

respectively.

Figure 1 shows the chromatograms of the resolution of $[Cr(acac)_3]$ by using methanol and methanol-water (80/20) as eluents. When methanol was used, the complex was partially resolved in a short time on a short column and a separation factor α[11] was found to be 1.28. Complete separation was attained with a longer column of 75-cm length. Methanol-water (80/20) was a better eluent and nearly base-line separation was observed with a short column. The α value was increased to 1.33, indicating that chiral recognition by (+)-PTrMA is enhanced by a more polar eluent.

$[Co(acac)_3]$ was better resolved than $[Cr(acac)_3]$ on the (+)-PTrMA column. The α values with methanol and methanol-water (80/20) systems were 1.32 and 1.37, respectively.

The CD and optical rotations were measured without purification of the resolved complexes after exchanging the solvent from methanol to benzene. The optical purities of the complexes were confirmed to be nearly 100% by HPLC and the concentrations of the samples were estimated spectrophotometrically on the basis of ε=492 (373 nm) of (±)-$[Cr(acac)_3]$ and ε=446 (400 nm) of (±)-$[Co(acac)_3]$ in benzene.[12] The first-eluted isomers of $[Cr(acac)_3]$ and $[Co(acac)_3]$ were found to be Δ-isomers from the CD spectra (Fig. 2).[13] The molar rotations $[M]^{25}$ of optically pure Δ-$[Cr(acac)_3]$ were estimated to be -4900° (546 nm) and -10600° (589 nm) in benzene ($C \approx 0.01$ g/dl) and those of Δ-$[Co(acac)_3]$ were +27400° (546 nm) and -6700° (589 nm) in the same solvent ($C \approx 0.01$ g/dl). These rotation values are close to the published data.[2,14,15]

The chiral discrimination of Δ- and Λ-isomers by (+)-PTrMA is probably done through the nonpolar interaction between the acetylacetonato propellers of the complexes and the triphenylmethyl propellers of the polymer (Fig. 3). The results of chromatography indicate that the Λ-isomers interact more strongly with the (+)-PTrMA. Inspection of the molecular models of a Λ-isomer and a triphenylmethyl group suggests that a Λ-isomer likely interacts more tightly with a left-handed triphenylmethyl propeller by superimposing its three propeller blades simultaneously on the phenyl groups. Concequently, the triphenylmethyl groups in (+)-PTrMA may adopt the same left-handed propeller as the Λ-isomers.

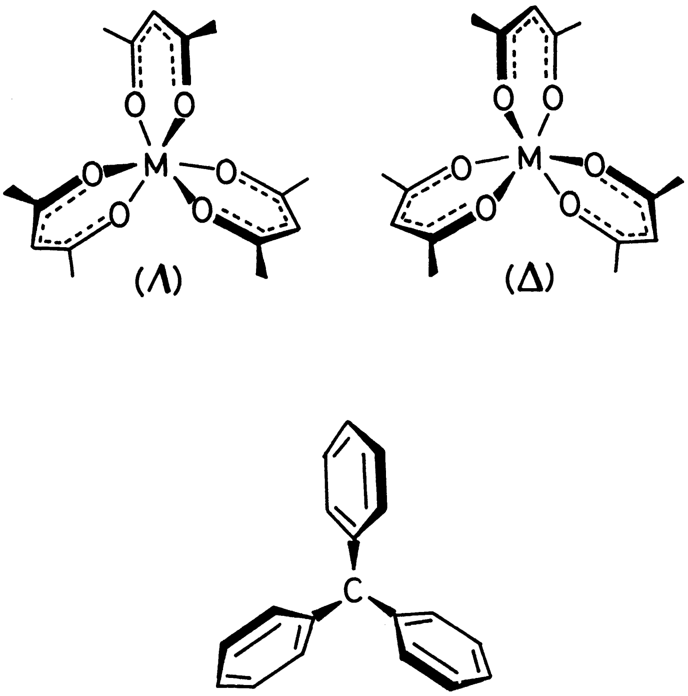

Fig. 3. Structures of Λ- and Δ-tris(acetylacetonato)M(III) and left-handed propeller of triphenylmethyl group.

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11) α = (retention volume of more retained enantiomer - void volume) / (retention volume of less retained enantiomer - void volume). The void volume was 3.3 ml.

12) The resolved enantiomers contain a trace amounts of contaminants from the (+)-PTrMA column. Their influences on the present optical data are negligible.

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