

## Chromatographic Resolution of Tris(acetylacetonato)aluminium(III) on an Optically Active Poly(triphenylmethyl Methacrylate) Column

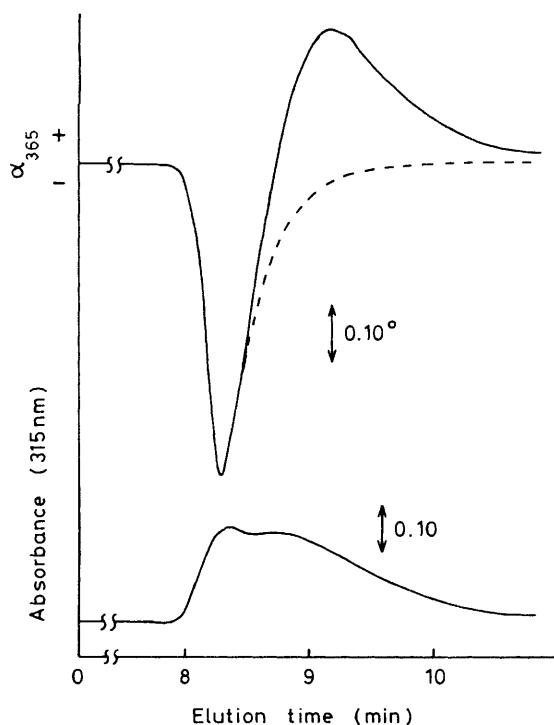
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Tris(acetylacetonato)aluminium(III) was resolved for the first time by h.p.l.c. on a (+)-poly(triphenylmethyl methacrylate) column, and the circular dichroism spectrum and racemization rates of one of the optical isomers were measured.

Although a great number of papers have been published on the resolution of octahedral complexes containing three bidentate ligands, none of them described the resolution of the complexes containing group 3B elements, Al, Ga, In.<sup>1</sup> The difficulty in resolving them is almost certainly due to rapid racemization at room temperature.<sup>2</sup> Previously, we reported

that optically active poly(triphenylmethyl methacrylate) (PTrMA) coated on macroporous silica gel is an efficient packing material for high-performance liquid chromatographic resolution (h.p.l.c.) of not only a wide variety of organic compounds<sup>3</sup> but also tris(acetylacetonato)-cobalt(III) and -chromium(III).<sup>4</sup> In this communication, we describe the



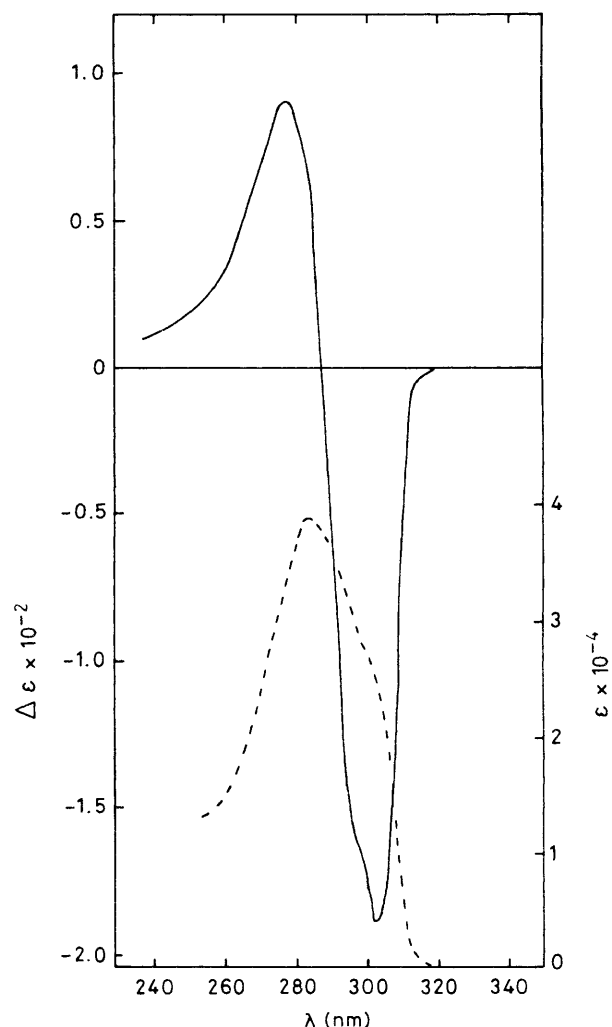
**Figure 1.** Resolution of  $[\text{Al}(\text{acac})_3]$  on (+)-PTTrMA (solid line); broken line represents the decrease of  $\alpha_{365}$  at  $26^\circ\text{C}$  when the flow of eluant into the flow cell was stopped at the maximum negative rotation. Column,  $50 \times 72$  (i.d.) cm; eluant, methanol (flow rate 2.50 ml/min); temperature,  $5^\circ\text{C}$ .

first resolution of tris(acetylacetonato)aluminium(III)  $[\text{Al}(\text{acac})_3]$  by h.p.l.c. on the chiral polymer.

The preparation of (+)-PTTrMA<sup>5</sup> and the polymer-coated silica gel<sup>3</sup> for h.p.l.c. were as reported previously. The chromatography was accomplished on a JASCO TRI ROTAR-II equipped with JASCO UV-100-III (315 nm, 0.1 cm cell) and DIP-181 polarimeter (365 nm) detectors using methanol as eluant, a stainless steel flow cell  $[50 \times 3$  (i.d.) mm] with optical windows being used for the polarimeter. The circular dichroism (c.d.) was measured with a 1 cm cell on a JASCO J40 c.d. apparatus.

Figure 1 shows the chromatogram of the resolution of  $[\text{Al}(\text{acac})_3]$  conducted at  $5^\circ\text{C}$ . The u.v. detector shows two peaks; the (-)-isomer was eluted first followed by the (+)-isomer. The flow of eluant into the flow cell for the polarimeter was stopped when it showed the maximum negative rotation and the decrease of the optical rotation was followed to estimate racemization rate. Rapid racemization proceeded {first-order with respect to (-)- $[\text{Al}(\text{acac})_3]$ } and its half-life period was an estimated 13 s at  $26^\circ\text{C}$ . The rate of racemization of (-)- $[\text{Al}(\text{acac})_3]$  collected in an optical cell was also measured at 0 and  $10^\circ\text{C}$  on the c.d. apparatus (303 nm), half-life periods being determined to be 434 and 98 s, respectively. The activation energy was estimated to be 22 kcal/mol (1 kcal = 4.18 kJ) which is close to the energy reported for the intramolecular interchange of trivalent aluminum complexes.<sup>6</sup>

The (-)<sub>365</sub>-complex eluted from the column was collected at  $-78^\circ\text{C}$  and its u.v. and c.d. spectra were measured in methanol at  $-78^\circ\text{C}$  (Figure 2). The c.d. spectral pattern is very similar to those of  $\Delta$ -(-)<sub>589</sub>-tris(acetylacetonato)-germanium(IV)<sup>7</sup> and -silicon(IV)<sup>8</sup> whose absolute configuration has been estimated from the assignment of the  $\pi \rightarrow \pi^*$  transition of lowest energy in the acetylacetonate ion respon-



**Figure 2.** U.V. (---) and c.d. (—) spectra of the (-)<sub>365</sub>-isomer of  $[\text{Al}(\text{acac})_3]$  eluted first, in methanol at  $-78^\circ\text{C}$  (path length of cell, 1 cm).

sible for the observed c.d. bands. thus, (-)<sub>365</sub>- $[\text{Al}(\text{acac})_3]$  is likely to be the  $\Delta$ -isomer. In the resolution of  $[\text{Cr}(\text{acac})_3]$  and  $[\text{Co}(\text{acac})_3]$  on the (+)-PTTrMA column,  $\Delta$ -isomers were also eluted in the first fractions.<sup>4</sup>

The chromatography at lower temperatures on PTTrMA appears to be a useful method for resolving more unstable trisacetylacetonatemetall(III) complexes and  $\Delta$ -isomers may be eluted first.

Received, 30th April 1984; Com. 600

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