

# OLIGOMERS OF Cr(ACAC)<sub>3</sub> AS A CHIRAL DOPANT INDUCING CHIRAL NEMATIC PHASES

Akihiko Yamagishi,<sup>1,2,\*</sup> Yuka Furuno,<sup>3</sup> Hisako Sato,<sup>1,2</sup> Yutaka Fukuda<sup>3</sup> and Naomi Hoshino-Miyajima<sup>4</sup>

<sup>1</sup>*Department of Earth and planetary Science, Graduate School of Science, The University of Tokyo, Tokyo 113 0033,* <sup>2</sup>*CREST, Japan Science and Technology Corporation,* <sup>3</sup>*Department of Chemistry, Ochanomizu University,* <sup>4</sup>*Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060 0810, Japan*

E-mail: [yamagisi@eps.s.u-tokyo.ac.jp](mailto:yamagisi@eps.s.u-tokyo.ac.jp)

## **Introduction**

A tris(acetylacetonato)metal(III) complex is known to act as an efficient chiral dopand due to its helical coordination structure. Motivated by this fact, we have been trying to develop a dopant based on acetylacetonato complexes. In the present work, the oligomers of Cr(acac)<sub>3</sub> have been synthesized and resolved chromatographically. Helical twisting power was attempted to be measured in order to see the linkage effect of chiral units on the ability of inducing chiral nematic phases.

## **Experimental and Results**

Oligomerization of Cr(acac)<sub>3</sub> was performed in a solid reaction. A 1:1 solid mixture of Cr(acac)<sub>3</sub> and taet (Figure 1) was placed in a Teflon vessel and kept at 160 °C for 12 hours. The fused product was dissolved in benzene and eluted on a silica gel column with 4:1 benzene/acetonitrile. From the mass spectral analyses, the first band was identified to be an unreacted Cr(acac)<sub>3</sub> and the second and third bands were assigned to be both dimers. The oligomers up to pentamers were confirmed to exist in more retained bands. Two band fractions corresponding to dimers (denoted by F2A and F2B, respectively) were eluted on a chiral column (Ceramosphere, Shiseido Co., Japan) with methanol. Fraction F2A gave two separated peaks as shown in Figure 2, while fraction F2B gave only one peak. From the CD spectra, the first and second peaks of fraction F2A were assigned to be  $\Lambda\Lambda$ - and  $\Delta\Delta$ -dimers, respectively (Figure 3). The single peak of fraction F2B gave no CD absorption, implying that it was  $\Delta\Delta$ -dimer (meso-type). The fraction corresponding to the trimer was also eluted on the same chiral column with methanol/chloroform, giving at least three peaks. From the CD spectra, the first and last peaks were suspected to be assigned to  $\Lambda\Lambda\Lambda$ - and  $\Delta\Delta\Delta$ -trimers, respectively.

The resolved enantiomers (monomers, dimers and trimers) were dissolved in MBBA. The pitch measurements were performed by the Cano method. The helical sense was determined from the measurements of induced CD spectra. The details of the results will be given and discussed.

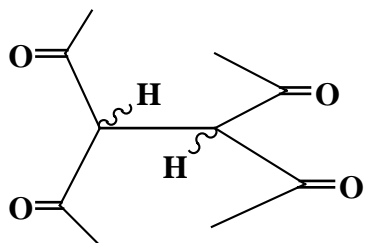


Figure 1. The structure of a bridging ligand (denoted by "taet")

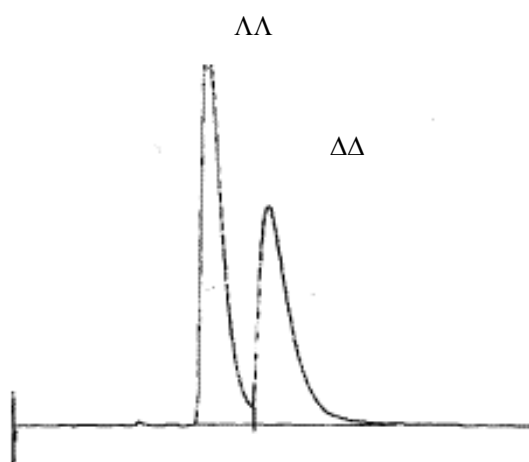


Figure 2 The chromatogram when a fraction corresponding to a dimer was eluted on a chiral column.

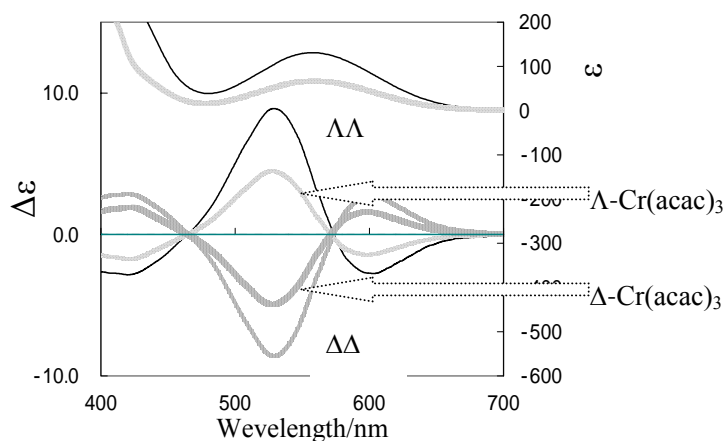


Figure 3. The UV (upper) and CD (lower) spectra of the enantiomers of monomer and dimers.