

Chiral Bead-like Trimer of Tris(2,4-pentanedionato)ruthenium(III)

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A chiral tri-nuclear metal complex, $\Delta\Delta\Delta$ - or $\Lambda\Lambda\Lambda$ - $[\text{Ru}(\text{acac})_2(\text{taet})\text{Ru}(\text{acac})(\text{taet})\text{Ru}(\text{acac})_2]$ (acac = acetylacetonato and taet = tetraacetyleanato), was prepared and its monolayer behavior was investigated, leading to the conclusion that the bead-like character of the trimer was an essential factor in achieving stable two-dimensional molecular packing.

Recently, molecular arrays of conjugated organic compounds have attracted extensive attention as possible candidates for conducting wires.^{1,2} The wire-like character of molecular assemblies is expected to amplify an electrical signal for sensing.^{3,4} When such an attempt is extended to metal complexes, it may open the possibility of coupling the array character with the electronic or magnetic properties intrinsic to metal ions.⁴⁻⁹

In the present work, we report the preparation of a chiral trimer linked by tetraketonato groups as the bridging ligands and investigate its monolayer behavior in a Langmuir–Blodgett (LB) film. Instead of using an amphiphilic ligand,¹⁰ the present work employed a bead-shaped multi-nuclear complex. It was expected that the bead-like properties might help the molecule align at an air–water interface similar to an amphiphilic molecule. For this purpose, multi-nuclear complexes were synthesized by one-pot reactions between a metal complex monomer and a linking ligand in a solid matrix. It has been demonstrated that the trimer of tris(acetylacetonato)ruthenium(III) thus prepared forms a reversible monolayer at an air–water interface. Notably no such stable monolayer forms for a monomer or a dimer. Thus, it was concluded that the bead-like character was essential to the formation of stable two-dimensional molecular packing. A molecular film consisting of such bead-shaped molecules might be a first step for forming molecular wires on a solid surface.

The crude product obtained after the reaction of $[\text{Ru}(\text{acac})_3]$ (acac = acetylacetonato) and tetraacetyleano (taetH₂) was eluted on a silica gel column with acetonitrile–benzene. As a result, oligomers up to the tetramer were separated as confirmed from mass spectral analyses. The fractions corresponding to the dimer and the trimer were eluted again on a silica gel column. The dimer fraction was separated into two bands containing $\Delta\Delta/\Lambda\Lambda$ and $\Delta\Lambda$ (meso) diastereomers as already described elsewhere.⁷ The trimer fraction was separated into three bands. From the NMR spectra of these bands, the last band was found to contain a pure trimer of C_2 symmetry (see Supporting Information).¹² Thus, the species in that band was one of the $\Delta\Delta\Delta/\Lambda\Lambda\Lambda$ or $\Delta\Lambda\Delta/\Lambda\Delta\Lambda$ diastereomers. Resolution of the racemic mixtures of the monomer, the dimer, and the C_2 -symmetric trimer was carried out on a chiral column packed with an ion-exchange adduct of Δ - $[\text{Ru}(\text{phen})_3]^{2+}$ (phen = 1,10-

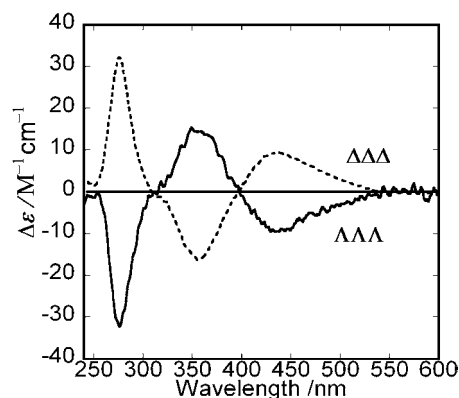
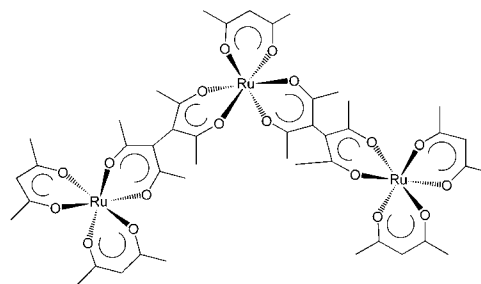


Figure 1. CD spectra of methanol solutions of resolved enantiomers: $\Lambda\Lambda\Lambda$ - (solid) and $\Delta\Delta\Delta$ - $[\text{Ru}(\text{acac})_2(\text{taet})\text{Ru}(\text{acac})(\text{taet})\text{Ru}(\text{acac})_2]$ (dotted). The vertical axis denotes $\Delta\epsilon$ per monomer unit.



Scheme 1. The molecular structure of a tri-nuclear metal complex ($\Delta\Delta\Delta$ - $[\text{Ru}(\text{acac})_2(\text{taet})\text{Ru}(\text{acac})(\text{taet})\text{Ru}(\text{acac})_2]$).

phenanthroline) and synthetic hectorite.¹¹ The eluting solvent was 4:1 (v/v) methanol–chloroform. The monomer and dimer were resolved into pure enantiomers with baseline separation. The trimer was resolved partially into two enantiomers. The circular dichroism spectra of the initial and final fractions are shown in Figure 1. From the spectral shapes and $\Delta\epsilon$, these fractions were concluded to contain $\Lambda\Lambda\Lambda$ - and $\Delta\Delta\Delta$ -trimers, respectively (see Supporting Information) (Scheme 1).¹²

Monolayer behavior of the monomer, the dimer, and the trimer was investigated at an air–water interface. In the case of the monomer, a chloroform solution of Δ - $[\text{Ru}(\text{acac})_3]$ was spread onto pure water. No surface pressure appeared upon compressing the surface to less than $0.1 \text{ nm}^2 \text{ molecule}^{-1}$. The same results were obtained for Λ - $[\text{Ru}(\text{acac})_3]$. These results indicated that the enantiomeric monomer dissolved in water before the compression of the surface. This was reasonable since the monomer dissolved in water to the concentration of 0.4 mM at 20°C . In the previous experiment, a stable monolayer was formed only

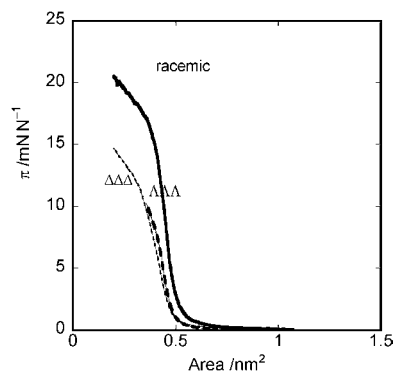
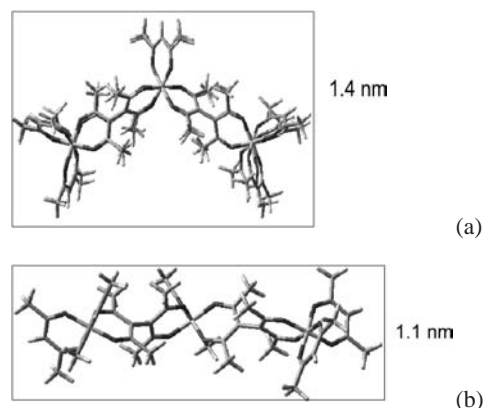


Figure 2. The π - A curves when a racemic mixture (solid line) or a pure enantiomer (dotted and broken line) of trimers was spread onto the subphase of pure water. The horizontal axis is the area per monomer unit.

when the acac ligand was made more hydrophobic by replacing the methyl groups with longer alkyl chains.¹⁰

In the case of the dimer, a chloroform solution of $\Delta\Delta$ -[Ru(acac)₂(taet)Ru(acac)₂] was spread onto a water phase. Surface pressure appeared upon compressing the surface to 0.1 nm² molecule⁻¹. The magnitude of the surface pressure was, however, lacking in reproducibility. It fluctuated between 10 and 20 nm² molecule⁻¹. Since the solubility of $\Delta\Delta$ -[Ru(acac)₂(taet)Ru(acac)₂] in water was less than 1 × 10⁻⁶ M at 20 °C, the dissolution of the dimer was thought to be negligible. This suggested that the dimer aggregated to form a solid particle at the air-water interface instead of forming a stable molecular film. The same results were obtained for $\Lambda\Lambda$ -[Ru(acac)₂(taet)Ru(acac)₂]. In the case of the trimer, a chloroform solution of $\Delta\Delta\Delta$ -[Ru(acac)₂(taet)Ru(acac)(taet)-Ru(acac)₂] was spread onto a water phase. A clear π - A curve was obtained as shown in Figure 2, in which the horizontal axis denotes the area per monomer unit. According to the results, surface pressure appeared around 0.7 nm² and rose steeply below the region of 0.5 nm². The curve showed a saturating tendency below 0.3 nm². Nearly the same curve was obtained for $\Lambda\Lambda\Lambda$ -[Ru(acac)₂(taet)Ru(acac)(taet)Ru(acac)₂]. In the case of the racemic mixture of the trimer, surface pressure had already appeared at 1.0 nm². The pressure rose steeply around 0.5 nm², remaining higher than that for the enantiomeric trimer across the entire region. Comparing the π - A curves between the enantiomer and the racemic mixture, it was deduced that the racemic mixture formed a more rigid molecular film within the same molecular area.

A floating monolayer of the trimer was deposited onto mica at an area of 0.40 nm² per monomer unit. The transfer ratio was 0.6 ± 0.1 for both enantiomeric and racemic trimers in the upward direction. The low value of the transfer ratio arose from the fact that the monolayer was hydrophobic and was repelled from the hydrophilic mica surface. The surface of the deposited films was observed with an AFM microscope (see Supporting Information).¹² From the AFM observations, the racemic molecules were concluded to be more upright from the substrate surface than the enantiomeric molecules. This was in accord with the situation that the racemic monolayer exhibited higher surface pressure than the enantiomeric one at the same value



Scheme 2. Models of molecular packing of racemic (a) and enantiomeric (b) trimers.

of molecular area as seen from their π - A curves (Figure 2). Thus, the effect of chirality was manifested in terms of different molecular orientations in a two-dimensional arrangement. The possible orientations of the molecule are shown in Scheme 2. Under these orientations, the area occupied by one monomer unit was estimated to be 0.88 and 0.72 nm² for racemic and enantiomeric trimers, respectively. These values are close to the area per monomer unit (0.6–0.8 nm²) when surface pressure began to increase from zero in the π - A curves.

The present work has demonstrated that the chiral bead-like metal complex exhibits a chirality effect on molecular packing in films. This finding may suggest that chirality can be a useful factor in controlling the molecular arrangement in films.

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- 12 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.esj.jp/journals/chem-lett/>.