Stereochemical Effects on Monolayer Formation of Racemic and Enantiomeric $[Ru(dpp)_3]^{2+}$ (dpp = 4,7-diphenyl-1,10-phenanthroline) at an Air–Water Interface

Yasutomo Goto, Masayuki Takahashi, Masahiro Taniguchi and Akihiko Yamagishi*

Department of Polymer Science, College of Science, Hokkaido University, Sapporo 060, Japan

Monolayer formation at an air–water interface is compared between enantiomeric and racemic $[Ru(dpp)_3]^{2+}$ (dpp = 4,7-diphenyl-1,10-phenanthroline), leading to the conclusion that the racemic mixture forms a more compact monolayer than the enantiomer.

We wish to report a novel attempt to observe the stereochemical effects on monolayer formation of a chiral metal complex at an air–water interface. Although the investigation of metal complex monolayers and Langmuir–Blodgett (LB) films is a currently active field,[1–4] there has been no report of phenomena involving a chiral metal complex.[5] In the course of comparing the surface properties of racemic and enantiomeric $[Ru(dpp)_3]^{2+}$ (dpp = 4,7-diphenyl-1,10-phenanthroline) complexes, the racemic mixture is revealed to form a more compact monolayer than the enantiomer.

Resolution of $[Ru(dpp)_3]^{2+}$ was performed by adding sodium antimonyl tartrate to a water–ethanol solution (1 : 1, v/v) of the racemic mixture. Δ-$[Ru(dpp)_3]^{2+}$ was filtered off as an insoluble antimonyl tartrate salt. Λ-$[Ru(dpp)_3](ClO_4)_2$ was obtained by adding an excess of sodium perchlorate to the filtrate. By measuring the circular dichroism spectrum of an ethanol solution of each enantiomer, $\Delta\varepsilon$ at 480 nm was determined to be -21 and 21 for Δ- and Λ-$[Ru(dpp)_3]^{2+}$, respectively. The NMR spectrum of a $CDCl_3$ solution of Λ-$[Ru(dpp)_3](ClO_4)_2$ in the presence of a shift reagent, tris{3-(heptafluoropropylhydroxymethylene)-(+)-camphorato}-europium(III) (Aldrich), confirmed that the content of Δ-$[Ru(dpp)_3](ClO_4)_2$ was negligible. A surface pressure–area per molecule curve was obtained at 25 °C after speading a chloroform solution of rac- or Λ-$[Ru(dpp)_3](ClO_4)_2$ on a subphase of an aqueous 0.1 mol dm^{-3} $NaClO_4$ solution. The rate of compression was 90 cm^2 min^{-1}.

The results are shown in Fig. 1. For Λ-$[Ru(dpp)_3](ClO_4)_2$ [curve (*a*)], the surface pressure (π) starts to rise at 300 $Å^2$ $molecule^{-1}$ (denoted by A_l); π continues to rise until the isotherm exhibits a complicated behaviour with maxima and minima above 30 mN m^{-1}. When the experiment was repeated on a fresh sample, the isotherm gave the same response within experimental error (± 10 $Å^2$ $molecule^{-1}$). The curve is, however, not reproducible in the region above 30 mN m^{-1}, giving maxima and minima at different surface areas. When a second isotherm was measured 1 h after the initially compressed sample was expanded, π rose at a value as low as A_l = 130 $Å^2$ $molecule^{-1}$. The drastic decrease of A_l may imply that the complex forms microcrystallites once it is compressed to a collapsed state.[6] For *rac*-$[Ru(dpp)_3](ClO_4)_2$ [curve (*b*)], π rises at A_l = 210 $Å^2$ $molecule^{-1}$ *i.e.* at an appreciably smaller value than for the enantiomer. In this case, too, the isotherm is reproducible only in the region less than 30 mN m^{-1}.

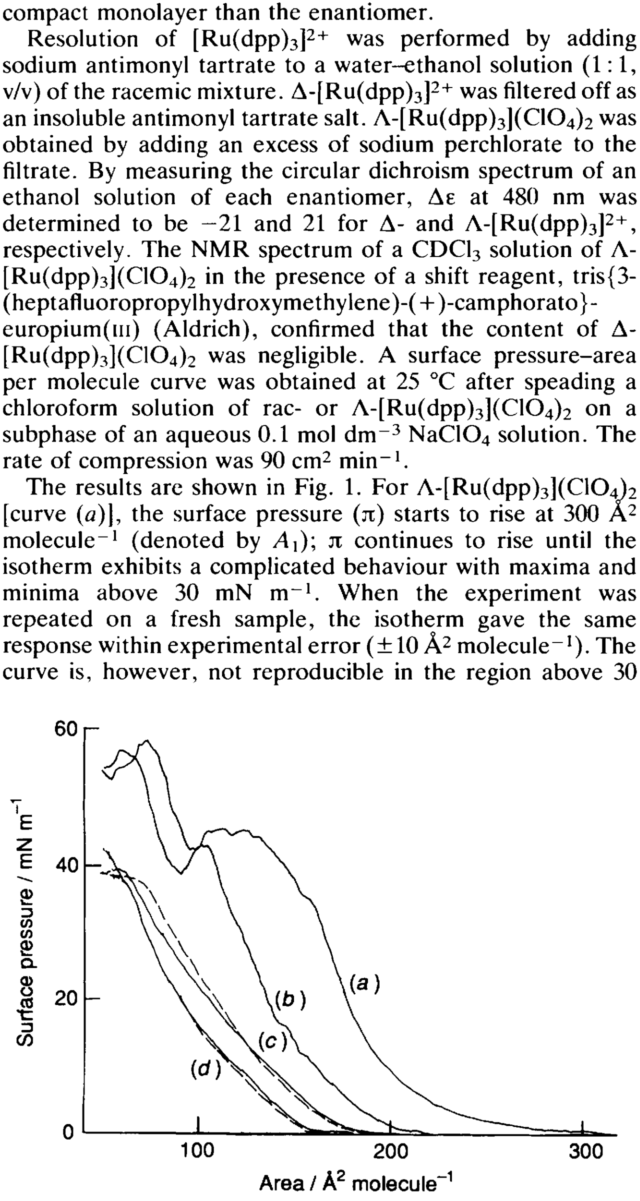

Fig. 1 Surface pressure–area per molecule isotherms for (*a*) Λ- and (*b*) *rac*-$[Ru(dpp)_3](ClO_4)_2$ and for 1 : 1 mixtures with stearic acid [(*c*) and (*d*)]. Dotted curves represent isotherms recorded 1 h after the initial measurements. Curves (*a*) and (*b*) in water in the presence of 0.1 mol dm^{-3} $NaClO_4$, (*c*) and (*d*) in pure water, T = 25 °C.

According to a space-filling molecular model, $[Ru(dpp)_3]^{2+}$ occupies an area of *ca.* 300 $Å^2$ (denoted by the theoretical limiting area) when it rotates freely on a water surface. The value of A_l for the enantiomer almost coincides with the theoretical limiting area, while A_l for the racemic mixture is much smaller. Thus the enantiomers repulse each other when they are in contact, while the racemic mixture forms a more dense monolayer probably with the phenyl groups of the facing ligands closely stacked.

Additional experiments were performed by spreading a 1 : 1 mixture of $[Ru(dpp)_3](ClO_4)_2$ and stearic acid in chloroform solution on pure water. As shown by the solid curves (*c*) and (*d*) in Fig. 1, A_l was found to be 150 and 170 $Å^2$ $molecule^{-1}$ for the racemic mixture and the enantiomer, respectively. Nearly reproducible isotherms were obtained in both cases when the same samples were compressed again (dotted curves). The results indicate that the racemic mixture forms a more compact monolayer than the enantiomer even in the presence of stearic acid.

X-Ray diffraction patterns were obtained for LB films of 1 : 1 mixtures of $[Ru(dpp)_3](ClO_4)_2$ and stearic acid which were transferred at 25 mN m^{-1} on a hydrophobic quartz surface to give 50-molecule thick layers. From the d(001) diffractions, the interlayer distance was found to be 50.0 and 37.6 Å for the racemic and enantiomeric metal complexes, respectively. These values can be compared with interlayer distance of a LB film of stearic acid alone (41.9 Å). Although the detailed structures of the present LB films are as yet unclear, the results indicate that the molecular packing in a LB film is dependent on the chirality of the complex. The stereochemical effects observed here may open a way to control the packing of amphiphilic molecules in a molecular layer by use of chirality.

Received, 4th March 1994; Com. 4/01313A

References

1 G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsh and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 4947.
2 X. Zhang and A. J. Bard, *J. Phys. Chem.*, 1988, **92**, 5566.
3 T. Nakamura, H. Tanaka, K. Kojima, M. Matsumoto, H. Tachibana and Y. Kawabata, *Thin Solid Films*, 1989, **179**, 183.
4 T. Richardson, G. G. Roberts, M. E. Polywka and S. G. Davies, *Thin Solid Films*, 1989, **179**, 405.
5 Chirality effects on monalayer formation of organic molecules have been reported in several papers: J. G. Heath and E. M. Arnett, *J. Am. Chem. Soc.*, 1992, **114**, 4500 and references cited therein; C. J. Eckhardt, *Nature*, 1993, **362**, 614.
6 C. J. Miller, P. McCord and A. J. Bard, *Langmuir*, 1991, **7**, 2781.