JOURNAL OF Materials CHEMISTRY

Resolution of optically active tris- and bis(diketonato)metal(III) complexes and their monolayer properties at an air–water interface

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Received 26th May 1998, Accepted 7th July 1998

The monolayer properties of tris- and bis(diketonato)metal(III) complexes were investigated at the air–water interface. The following eight complexes were synthesized: [Cr(acacNO$_2$)$_3$] (acacNO$_2$ = 3-nitropentane-2,4-dionato), [Co(acacNO$_2$)$_3$], [Ru(PHE)$_3$] (PHE = 1,3-diphenylpropane-1,3-dionato), [Ru(HPD)$_3$] (HPD = heptane-3,5-dionato), [Ru(NND)$_3$] (NND = nonane-4,6-dionato), [Ru(DMH)$_3$] (DMH = 2,6-dimethylheptane-3,5-dionato), *fac*-[Ru(acacF$_3$)$_3$] (acacF$_3$ = 1-1,3-bis(trifluoromethyl)propane-1,3-dionato) and [Ru(acac)$_2$(PHE)]. When these complexes were eluted with a methanol–chloroform mixture on a column packed with Δ-[Ru(phen)$_3$]$^{2+}$/laponite, resolution was achieved for [Cr(acacNO$_2$)$_3$], [Co(acacNO$_2$)$_3$], [Ru(HPD)$_3$], [Ru(NND)$_3$] and [Ru(acac)$_2$(PHE)]. To study the monolayer behavior, a chloroform solution of a ruthenium(III) complex was spread onto a water surface and a surface pressure–molecular area (π–A) curve was measured. The π–A curves for [Ru(DMH)$_3$], *fac*-[Ru(acacF$_3$)$_3$] and [Ru(NND)$_3$] were reversible. The π–A curves for other compounds displaced irreversibly towards smaller molecular areas on the second compression, indicating that the compounds formed microcrystallites under high surface pressure. In the case of [Ru(NND)$_3$], the stereochemical effects on monolayer formation were studied by comparing the π–A curves between a racemic mixture and an enantiomer. As a result, the racemic mixture of the complex was found to form a more compact monolayer than the pure enantiomer.

Recently the monolayers and thin films of metal complexes are attracting attention as functional molecular assemblies such as sensors, pyroelectric and non-linear optical materials.[1–3] The development of these two-dimensional assemblies as molecular devices depends on the knowledge of the packing structures of the component molecules. Little is known, however, about the stereochemical effects on the packing of chiral metal complexes in a monolayer state. This is in contrast with the enormous amount of knowledge which has been accumulated on the packing of metal complexes in solid crystals.[4] We have previously studied the chiral aggregation phenomena when optically active metal complexes are intercalated in layered inorganic compounds like clays.[5–7] We wish to extend our results to more general systems, such as monolayers of chiral metal complexes at the air–water interface and Langmuir–Blodgett (LB) films.

We have previously reported studies on the stereochemical effects of tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) and bis(acetylacetonato-3-dodecylacetylacetonato)ruthenium(III) for a monolayer and an LB film.[8,9] The present investigation has focused on the monolayer properties of tris- and bis(diketonato)metal(III) complexes. These complexes are chiral due to the asymmetric coordination of a central metal(III) ion. In our laboratory, the chromatographic method to resolve tris(acetylacetonato)metal(III) has been developed by use of an ion-exchange adduct of a clay with optically active metal complexes.[7] Tris(acetylacetonato)metal(III) does not form a monolayer because it is soluble in water. An analogous compound with hydrophobic diketonato ligands is, however, expected to form an insoluble monolayer. Such a series of compounds would provide a good example for a systematic study on the effect of molecular shape on the formation of a monolayer.

In this work, eight kinds of tris- or bis-chelated complexes were synthesized and their resolution was attempted. Fig. 1 shows six kinds of ligands used in the present study together with the molecular models of the tris-chelated complexes. We have examined the resolution capability of our column for these kinds of tris- and bis(diketonato)metal(III) complexes. The monolayer behavior of these complexes was studied at the air–water interface for a chloroform solution of each compound spread onto a water surface. Finally, by comparing the behavior of reversible monolayer formation for a racemic mixture and a pure enantiomer, the effects of homo- and hetero-chirality on molecular packing in the two-dimensional state were examined.

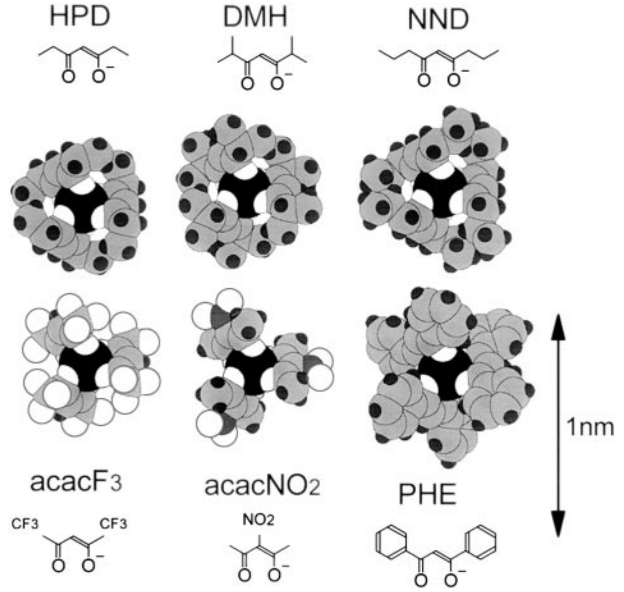

Fig. 1 The structures of the investigated ligands and the molecular models of tris-chelated complexes.

Experimental

Materials

[Cr(acacNO$_2$)$_3$] (acacNO$_2$ = 3-nitropentane-2,4-dionato) and [Co(acacNO$_2$)$_3$] were synthesized by nitrating tris(acetylacetonato)metal(III) with $Cu(NO_3)_2 \cdot 3H_2O$.[10] $[Ru(PHE)_3]$ (PHE = 1,3-diphenylpropane-1,3-dionato), $[Ru(HPD)_3]$ (HPD = heptane-3,5-dionato), $[Ru(NND)_3]$ (NND = nonane-4,6-dionato) and $[Ru(DMH)_3]$ (DMH = 2,6-dimethylheptane-3,5-dionato) were synthesized by adding the corresponding ligands (MERCK-Schuchardt) to a solution of Ruthenium Blue under a nitrogen atmosphere.[11] $[Ru(acac)_2(PHE)]$ was prepared by reacting $[Ru(acac)_2(CH_3CN)_2]$ with 1,3-diphenylpropane-1,3-dione in 1 : 1 (v/v) water–ethanol.[12] These compounds were all insoluble in water. The complexes were purified by column chromatography (Capcell Pack C18, Shiseido, Japan). The ruthenium content was determined by inductively coupled plasma spectrometry (ICP). For the ICP measurements, a sample solution was prepared by decomposing the ruthenium complex in concentrated nitric acid and diluting it with deionized water. *fac*-$[Ru(acacF_3)_3]$ ($acacF_3$ = 1,3-bis(trifluoromethyl)propane-1,3-dionato) was donated by Prof. K. Shimizu (Sophia University, Tokyo). The resolution of the ruthenium complexes was attempted by elution on a clay column (Chiral RU-1, Shiseido, Japan), with a chloroform–methanol mixture. The column was packed with synthetic hectorite ion-exchanged with Δ-$[Ru(phen)_3]^{2+}$.[7] As a result, $[Cr(acacNO_2)_3]$, $[Co(acacNO_2)_3]$, $[Ru(NND)_3]$, $[Ru(HPD)_3]$ and $[Ru(acac)_2(PHE)]$ were resolved. Other compounds were not resolved. All materials were of reagent grade and used without further purification. Water was purified with a membrane filter (Milli-Q SP Reagent Water System; Millipore).

Measurements

A surface pressure–area (π–A) curve was measured with a Langmuir trough (FSD-100, USI, Japan). The area of the trough was reduced from 130 cm^2 to 30 cm^2. Surface pressure was measured with a Whylhelmy balance. The compression rate was 10 cm^2 min^{-1}. The temperature was controlled by circulating water. A π–A curve was measured at 16 °C 30 minutes after a chloroform solution of the complex (*ca.* 5×10^{-4} M) was spread on the water. The compression–expansion procedure was repeated 2–4 times with an interval of 30 minutes each time. ICP measurements were performed with an ICP instrument (ICAP-575II, Nippon Jarrell-Ash, Japan). A circular dichroism (CD) spectrum was recorded with a spectropolarimeter (J-500, Jasco, Japan) at room temperature. Phase contrast microscopy observations were made with a phase contrast microscope (OPTIPHOT-2, Nikon, Japan) equipped with a CCD camera (Hamamatsu Photonics, Japan). Atomic force microscopy (AFM) measurements were performed with a Nanoscope III atomic force microscope (Digital Instruments) at ambient temperature. A 20 μm by 20 μm scan head and a silicon nitride tip on a cantilever with a spring constant of 0.12 N m^{-1} were used. The measurements were done in the 'force mode', in which the tip was scanned at constant height in measuring the spring deflection. A monolayer was transferred onto mica by the vertical dipping method in the upstroke direction at a speed of 5 mm min^{-1}. The transfer ratio was 0.90 in the case of racemic $[Ru(NND)_3]$.

Results

Resolution of diketonato complexes

A racemic mixture of $[Cr(acacNO_2)_3]$ was eluted with 1 : 3 (v/v) chloroform–methanol at 30 °C. Two peaks appeared in the chromatogram near to base-line separation. These peaks corresponded to the enantiomers of the compound. Fig. 2 shows the CD spectrum of the less retained isomer. Comparing the reported CD spectra of the enantiomers of $[Cr(acac)_3]$,[13] the configuration of the less retained isomer was assigned to be Δ.

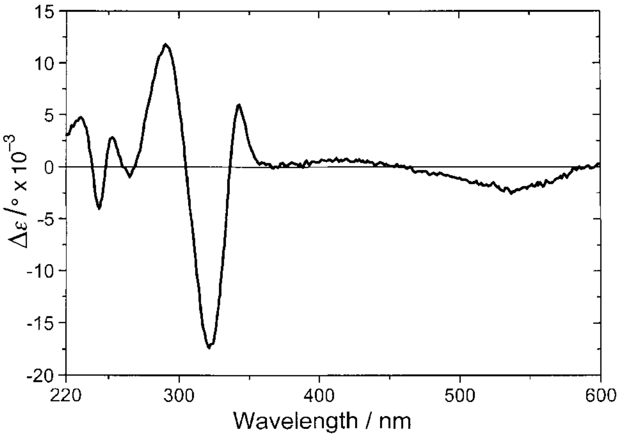

Fig. 2 The CD spectra of the less retained enantiomers when a racemic mixture of $[Cr(acacNO_2)_3]$ was eluted on a column packed with Δ-$[Ru(phen)_3]^{2+}$/laponite.

Resolution was attained for $[Cr(acacNO_2)_3]$, $[Co(acacNO_2)_3]$, $[Ru(NND)_3]$, $[Ru(HPD)_3]$ and $[Ru(acac)_2(PHE)]$ under the same conditions. Other compounds were not resolved. From the CD spectra of the resolved complexes, the configuration of the less retained isomer was assigned to be Δ for $[Cr(acacNO_2)_3]$ and $[Co(acacNO_2)_3]$, while it was Λ for $[Ru(NND)_3]$, $[Ru(HPD)_3]$ and $[Ru(acac)_2(PHE)]$. On the present column, chiral recognition was thought to be achieved through the intermolecular interactions between the diketonato complex and pre-adsorbed Δ-$[Ru(phen)_3]^{2+}$ on the clay surface.[7] Thus the observed stereoselectivity implied that the association mode of a diketonato complex with Δ-$[Ru(phen)_3]^{2+}$ is affected critically by the substituents on the acetylacetonato ligand. As an alternative method for the unresolved compounds, (2*R*,3*R*)-(−)-dibenzoyltartaric acid was added to a 1 : 2 (v/v) benzene–cyclohexane solution.[14,15] Although a precipitate was formed, no optical activity was detected either in the precipitate or in the filtrate.

General features of monolayer behavior

Fig. 3 summarizes the results of the repeated measurements of π–A curves when a chloroform solution of a compound was spread onto a pure water surface.

In the case of racemic $[Cr(acacNO_2)_3]$ {denoted by (A) *rac*-$[Cr(acacNO_2)_3]$}, the surface pressure increased at a molecular area of 0.15 nm^2 $molecule^{-1}$, which is much smaller than the cross-sectional area of the complex (0.6 nm^2 $molecule^{-1}$). On the second compression, the curve was displaced remarkably towards smaller molecular area. The third and fourth compression curves were displaced further. The results indicated that the compound did not form a reversible monolayer. In the case of Δ-$[Cr(acacNO_2)_3]$, the lift-off area on the first compression was 0.10 nm^2 $molecule^{-1}$, which was smaller than that for the racemic mixture (not shown). The π–A curve also showed an irreversible change on the second compression. Nearly the same results were obtained for racemic and enantiomeric $[Cr(acacNO_2)_3]$.

In the case of (B) *rac*-$[Ru(PHE)_3]$, the second and third compression curves were displaced towards the smaller molecular area than the first curve. The surface pressure rose from zero at about 3.2 nm^2 $molecule^{-1}$. An inflection point was observed at 30 mN m^{-1}. Fig. 4 shows the water surface observed with a phase contrast microscope at a molecular area of 4 nm^2 $molecule^{-1}$. Black spots with a diameter of less than 1 μm were present even under the conditions of zero surface pressure. This indicated that the molecules formed aggregates or microcrystallites immediately when they were spread on a water surface.

In the case of (C) *rac*-$[Ru(HPD)_3]$, the surface pressure rose at about 6 nm^2 $molecule^{-1}$ and increased very slowly to

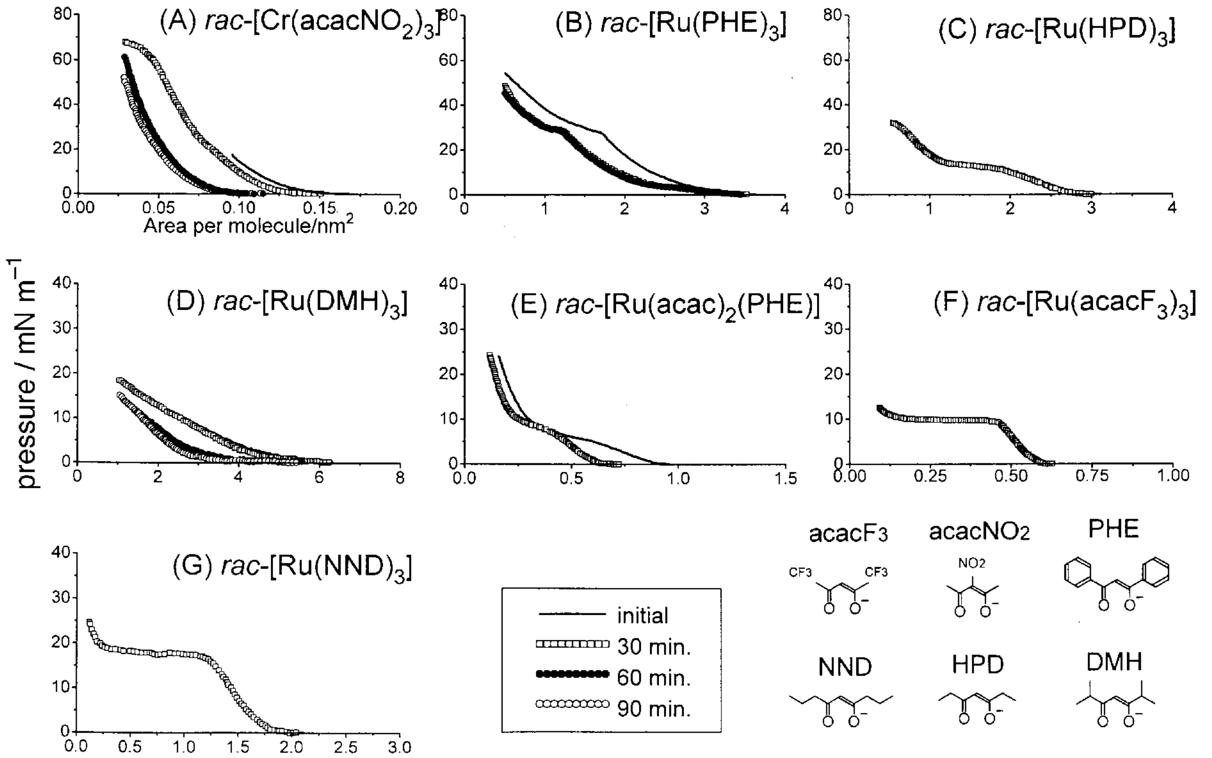

Fig. 3 The π–A curves of tris- or bis-diketonato metal(III) complexes spread on pure water at 16 °C. The figures denote the compression curves measured successively with an interval of 30 minutes: (A) racemic [Cr(acacNO$_2$)$_3$], (B) racemic [Ru(PHE)$_3$], (C) racemic [Ru(HPD)$_3$], (D) racemic [Ru(DMH)$_3$], (E) racemic [Ru(acac)$_2$(PHE)], (F) racemic [Ru(acacF$_3$)$_3$] and (G) racemic [Ru(NND)$_3$].

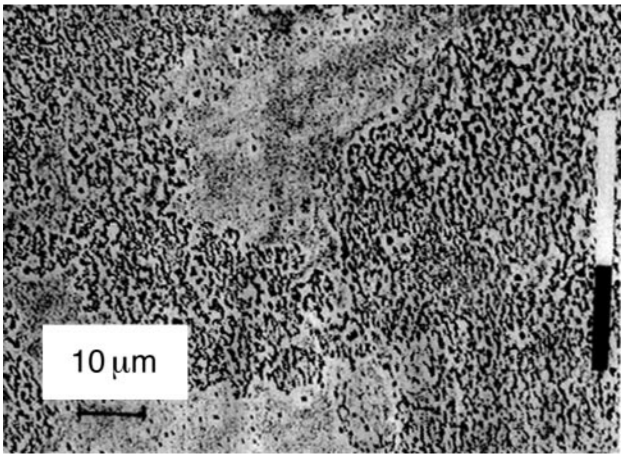

Fig. 4 The water surface observed with a phase contrast microscope at the molecular area of 4 nm^2 molecule^{-1} when a chloroform solution of racemic [Ru(PHE)$_3$] was spread on the surface.

1 nm^2 molecule^{-1}. A slight inflection was seen around 10 mN m^{-1}. The second compression curve was displaced a little towards smaller molecular area. The third and fourth compression curves were displaced further towards smaller molecular area.

In the case of (D) *rac*-[Ru(DMH)$_3$], the second compression curve nearly coincided with the first one, indicating that the complex formed a reversible monolayer. The lift-off area was 2.8 nm^2 molecule^{-1}. A plateau appeared at 10 mN m^{-1} in the range of 2.0–1.0 nm^2 molecule^{-1}. After passing the plateau region, the surface pressure increased steeply until it collapsed at 30 mN m^{-1}.

In the case of (E) *rac*-[Ru(acac)$_2$(PHE)], the surface pressure rose at 0.9 nm^2 molecule^{-1} and attained a plateau of 5 mN m^{-1} at 0.6 nm^2 molecule^{-1}. After passing the plateau region, the surface pressure rose steeply until it reached 25 mN m^{-1} at 0.2 nm^2 molecule^{-1}. The second compression curve was displaced markedly towards smaller molecular area.

In the case of (F) *rac*-[Ru(acacF$_3$)$_3$] the surface pressure rose at 0.6 nm^2 molecule^{-1} and attained a plateau of 10 mN m^{-1}. The plateau region continued until the molecular area reached 0.10 nm^2 molecule^{-1} where the surface pressure rose again. The second compression curve was slightly shifted towards smaller molecular area.

In the case of (G) *rac*-[Ru(NND)$_3$], the initial and second compression curves coincided completely. The surface pressure rose from zero at about 2.00 nm^2 molecule^{-1} and increased gradually until it attained the plateau of 19 mN m^{-1} at 1.20 nm^2 molecule^{-1}. The plateau continued up to 0.20 nm^2 molecule after which the surface pressure increased steeply. When the surface was observed with a phase contrast microscope, no black spots appeared at any stage of compression. This result implied that the compound formed a homogeneous monolayer.

Stereochemical effects on [Ru(NND)$_3$] monolayer formation

[Ru(NND)$_3$] formed a reversible monolayer. The monolayer behavior of this compound was studied in detail. Part (A) in Fig. 5 compares the π–A curves of Δ-, Λ- and *rac*-[Ru(NND)$_3$]. The curves of the Δ-and Λ-isomers were displaced towards larger molecular area than that of the racemic mixture. Accordingly the molecular area of the racemic mixture was about 7% smaller than that of each enantiomer at 10 mN m^{-1}. The results indicated that the racemic mixture formed a more compact monolayer than the pure enantiomer.

Part (B) in Fig. 5 shows the effect of temperature on the π–A curve of Δ-[Ru(NND)$_3$]. The curve was displaced towards smaller molecular area with increasing temperature. Concomitantly the surface pressure at the plateau region decreased with increasing temperature. Applying the thermodynamic equation to the results, the change of the surface pressure, $\Delta\pi$, at the plateau with temperature is expressed as

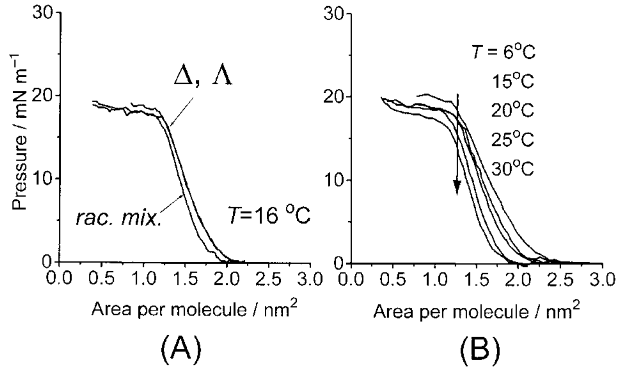

Fig. 5 (A) Stereochemical effects on the π–A curves of the Λ-, Δ-isomers and racemic mixture of $[Ru(NND)_3]$ at 16 °C. (B) Temperature effects on the π–A curves of $[Ru(NND)_3]$ for 6–30 °C.

below:[16]

$$d\Delta\pi/d\Delta T = \Delta S/\Delta A \qquad (1)$$

in which ΔS and ΔA denote the changes of entropy and molecular area, respectively, at the phase transition. Since the left-hand side and ΔA are negative, ΔS is positive. Thus the phase transition in the plateau region was accompanied by an increase of entropy. Since the plateau continued until the molecular area reached 0.2 nm^2 molecule^{-1}, the new phase after the transition might consist of multilayers containing at least 5–6 layers.

A monolayer of racemic $[Ru(NND)_3]$ was deposited on mica at 15 mN m^{-1}. AFM observation showed that the surface was rather flat with a thickness of 10–20 nm, which is regarded as the height of mono- or bilayers of $[Ru(NND)_3]$.

Chiral discrimination by a monolayer of $[Ru(NND)_3]$

A monolayer of chiral $[Ru(NND)_3]$ was formed on an aqueous solution containing a chiral ion, with the purpose to see chiral discrimination by a monolayer. Fig. 6 shows the effect of Δ-$[Ru(phen)_3]Cl_2$ in the subphase on the π–A curves of chiral $[Ru(NND)_3]$. Curve 1 is the π–A curve of Λ-$[Ru(NND)_3]$ on pure water. The curve of Δ-$[Ru(NND)_3]$ (not shown) was almost identical to curve 1. Curves 2 and 3 are the π–A curves of Λ- and Δ-$[Ru(NND)_3]$ respectively, when the subphase contained 8.3×10^{-5} M of Δ-$[Ru(phen)_3]Cl_2$. Both of the curves had a lift-off area of about 2.40 nm^2 molecule^{-1}, which is larger than that on a pure water subphase. The results implied that a cation, Δ-$[Ru(phen)_3]^{2+}$, was associated with $[Ru(NND)_3]$ to expand the monolayer. On compressing the area, the curve of Λ-$[Ru(NND)_3]$ approached that obtained on a pure water subphase, while the curve of Δ-$[Ru(NND)_3]$ stayed at a molecular area which was larger by about 0.2 nm^2 molecule^{-1}. The results indicate that Δ-$[Ru(phen)_3]$ was dissociated from Λ-$[Ru(NND)_3]$ on compression, but the same metal complex remained bound to the monolayer of Δ-$[Ru(NND)_3]$. Curves 4 and 5 are the π–A curves for Λ- and Δ-$[Ru(NND)_3]$, respectively, on a subphase containing 2.5×10^{-4} M of Δ-$[Ru(phen)_3]^{2+}$. Under these conditions, the curves were nearly the same, indicating that Δ-$[Ru(phen)_3]^{2+}$ remained bound to the monolayers irrespective of the chirality of $[Ru(NND)_3]$.

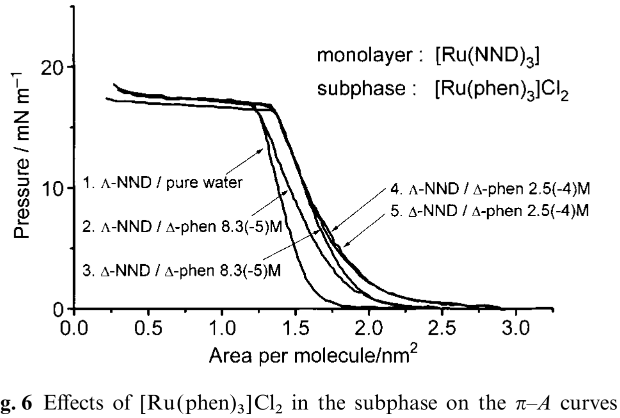

Fig. 6 Effects of $[Ru(phen)_3]Cl_2$ in the subphase on the π–A curves of chiral $[Ru(NND)_3]$ at 16 °C: (1) Λ-$[Ru(NND)_3]$ on pure water, (2) Λ-$[Ru(NND)_3]$ on a subphase of 8.3×10^{-5} M of Δ-$[Ru(phen)_3]Cl_2$, (3) Δ-$[Ru(NND)_3]$ on a subphase of 8.3×10^{-5} M of Δ-$[Ru(phen)_3]Cl_2$, (4) Λ-$[Ru(NND)_3]$ on a subphase of 2.5×10^{-4} M of Δ-$[Ru(phen)_3]Cl_2$, (5) Δ-$[Ru(NND)_3]$ on a subphase of 2.5×10^{-4} M of Δ-$[Ru(phen)_3]Cl_2$.

Discussion

Among the investigated eight compounds, $[Ru(DMH)_3]$, $[Ru(acacF_3)_3]$ and $[Ru(NND)_3]$ were found to form a reversible monolayer at the air–water interface. Other compounds did not show a reversible monolayer, probably because they formed a microcrystallite irreversibly on compressing a monolayer. As shown by the molecular models in Fig. 1, the tris-chelated complexes investigated in the present work are nearly spherical in shape. Some organic compounds of a spherical shape, like C_{60}, are also known to form a rigid monolayer.[17] Thus it is not surprising that these tris(diketonato) complexes were capable of forming a monolayer under the cohesive energy appropriate conditions.

When three reversible π–A curves obtained for $[Ru(DMH)_3]$, $[Ru(acacCF_3)_3]$ and $[Ru(NND)_3]$ are compared (Fig. 3), it is noted that they have the following common characteristics. The surface pressure lifted off at a molecular area corresponding to the cross-section of a molecule. The surface pressure increased gradually with decreasing molecular area, indicating that the monolayer had liquid-like properties and was easy to compress. At a critical molecular area, the π–A curves reached a plateau region. The presence of such a plateau region was best interpreted in terms of the assumption that the monolayer underwent a phase transition. Since the plateau continued to molecular areas as small as 1–0.1 nm^2 molecule^{-1}, the monolayer was thought to convert into a multilayer at the transition. No structure was seen with phase contrast microscopy in the plateau region in the case of $[Ru(NND)_3]$. Thus the multilayer might be a fluid-like layer. This was in agreement with the thermodynamic analyses on the phase transition of $[Ru(NND)_3]$ [Fig. 5(B)]. According to this, the multilayer possessed more positive entropy than the monolayer. One possibility was that the propyl groups of $[Ru(NND)_3]$ were more freely rotating in the multilayer state than in the monolayer state. It is interesting that this molecule, the melting point of which is higher than room temperature, showed a liquid-like multilayer state already at 6 °C.

Fig. 5(A) indicates that the racemic mixture formed a more compact monolayer than either pure enantiomer. The facts are compared with the densities of crystals of tris(diketonato)-metal(III). In the crystalline state, racemic $[Cr(acac)_3]$ has a higher density (1.362 g cm^{-3}) than either enantiomer (1.285 g cm^{-3}).[18,19] Similarly racemic $[Ru(acac)_3]$ has a higher density (1.59 g cm^{-3}) than either enantiomer (1.1.476 g cm^{-3}).[20] In a racemic crystal, these compounds form a homochiral column of each enantiomer with the C_3 axes parallel.[18] The homochiral columns of Δ- and Λ-isomers are packed alternately. In an enantiomeric crystal, the molecules are stacked with their C_2 axes parallel.[19,20] Under this orientation, they do not attain a density as high as that of the racemic crystal. Since the monolayer density of $[Ru(NND)_3]$ exhibited the same stereochemical effects as the crystal, it is postulated that the molecules are packed in a way similar to the crystalline state.

The results in Fig. 6 provided evidence that a molecule in the monolayer state ($[Ru(NND)_3]$) interacts stereoselectively with a chiral ion in the subphase (Δ-$[Ru(phen)_3]^{2+}$). From the change of the π–A curves, it was concluded that the Δ-isomer of $[Ru(phen)_3]^{2+}$ bound to Δ-$[Ru(NND)_3]$ more strongly than to Λ-$[Ru(NND)_3]$. It is noted that this selectivity is the same as what was observed when $[Ru(NND)_3]$ was resolved on a column packed with an ion-exchange adduct of Δ-$[Ru(phen)_3]^{2+}$/laponite. Therefore the same chiral recognition mode was operative in both solid and monolayer states.

Previously the observed stereoselectivity for column chromatography was rationalized in terms of the association mode that Δ-$[M(acac)_3]$ and Δ-$[M(phen)_3]^{2+}$ were stacked with their three-fold symmetry axes parallel.[21] In such a conformation, the three methyl groups in Δ-$[M(acac)_3]$ are located above the phenanthroline ligands in Δ-$[M(phen)_3]^{2+}$. The present results suggest that similar stacking takes place at an air–water interface.

The authors express their thanks to Professor K. Shimizu (Sophia University) for donating a material and also to Professor K. Mukasa (Hokkaido University) for the measurements with a phase contrast microscope.

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Paper 8/03921F