

Interactions at the Molecular Level between Biphosphine Ruthenium Complexes and Stearic Acid in Langmuir and Langmuir–Blodgett Films

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A molecular-level interaction between biphosphine ruthenium complexes and stearic acid has been observed in Langmuir and Langmuir–Blodgett (LB) films. Similar results were obtained for the ruthenium complexes *mer*-[RuCl₃(dppb)(4-Mepy)] (dppb = PPh₂(CH₂)₄PPh₂; 4-Mepy = 4-methylpyridine) (Rupic) and *mer*-[RuCl₃(dppb)(py)], (pyridine) (Rupy), which differ by the substituent group in the pyridine ring. The interaction was manifested in the Langmuir films by a nonlinear increase in the area per molecule and in surface potential with the relative concentration of the ruthenium complex in the mixture. In the LB films, interaction with stearic acid occurred via complexation with Rupy or Rupic, even though the latter are not charged. It is suggested that one of the chlorides is labilized, thus promoting complexation and keeping the Ru(III) oxidation state for the complex. Complexation was confirmed through FTIR data. Interaction with stearic acid enhanced the color change characteristic of biphosphine ruthenium complexes, which may be associated with an order-induced effect or with the exposure to the water subphase in the LB film preparation. In addition, X-ray diffraction experiments failed to detect separate domains of cadmium stearate, which is also attributed to the molecular-level interaction that prevents separate stearic acid or cadmium stearate domains from being formed.

1. Introduction

The fabrication of supramolecular structures with molecular control using techniques such as the Langmuir–Blodgett (LB)^{1,2} or self-assembly² usually has a 2-fold aim. On one hand, structures may be envisaged in which control of molecular architecture is achieved. On the other hand, one might wish to exploit material properties in the ultrathin films that may be markedly different from those of the same material in other forms. Recent results in our laboratories have indicated that biphosphine ruthenium complexes display characteristics that are unique to their LB form. For instance, a color change was observed for LB films of biphosphine ruthenium complexes, such as *mer*-[RuCl₃(dppb)(4-Mepy)] (dppb = PPh₂(CH₂)₄PPh₂; 4-Mepy = 4-methylpyridine) (Rupic), in comparison with chloroform solutions and cast films of this compound.³ This color change probably appears because some ligand–Ru interactions only occur in anisotropic structures or if the material is exposed to an aqueous subphase. Electroactivity is observed in cyclic voltammetry for LB films of Rupic and *mer*-[RuCl₃(dppb)(py)], py = pyridine) (Rupy), while no detectable activity was noted in cast films of the same compounds.⁴ Again, the organized nature of the LB films appears to govern the final film properties to a large extent. In another work,⁵ incorporation of Rupy led to an increase in stability of the electrical response of polyaniline LB films.

There is evidence to suggest, particularly from the studies of the mixed polyaniline–Rupy films,⁵ that the prominent features

of LB films from biphosphine ruthenium complexes are associated with interactions at the molecular level. Investigation into these interactions is not straightforward, especially because ruthenium complexes are likely to form nonmonomolecular structures at the air–water interface owing to its nonamphiphilic nature. In this paper we investigate Langmuir and LB films from two ruthenium complexes, namely Rupic and Rupy, either pure or mixed with stearic acid. Motivation for this study is the possible use of LB films in heterogeneous catalysis,^{6,7} in chemical⁸ and biological sensors,⁹ and also in modified electrodes for electrocatalysis.^{10,11} The mixed films are fabricated within the philosophy of the mixed monolayer approach, in which the nonamphiphilic material is co-spread with a fatty acid to improve both film stability and transfer onto a solid substrate. The Langmuir monolayers are characterized by surface pressure and surface potential measurements, while the deposited LB films are investigated using FTIR and UV–vis spectroscopy and X-ray diffraction. The interaction of the ruthenium complexes with stearic acid is considerably different from those observed with nonamphiphilic materials such as conducting polymers,¹² lignins,^{13,14} and ytterbium bisphthalocyanine.¹⁵ On the basis of the analysis of experimental data for various relative concentrations of stearic acid and ruthenium complexes, we propose a mechanism for the interaction.

2. Experimental Procedures

The complexes Rupy and Rupic were prepared according to the procedures prescribed in ref 16; their structures are shown in parts a and b, respectively, of Figure 1. In addition to pure monolayers, mixed films containing Rupic or Rupy and stearic acid (SA) at several concentrations (1:3 Ru:SA, 1:1 Ru:SA, and 3:1 Ru:SA) were obtained. For comparison, monolayers from

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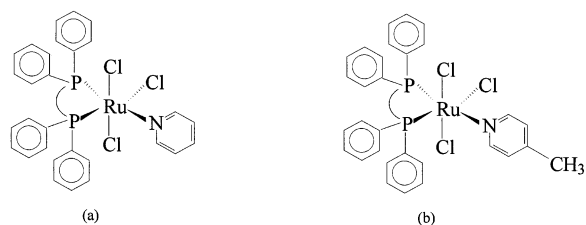


Figure 1. Structures of complexes *mer*-[RuCl₃(dppb)(py)], Rupy (a), and *mer*-[RuCl₃(dppb)(4-Mepy)], Rupic (b).

pure stearic acid were also obtained. Langmuir monolayers were spread from chloroform (Merck) solutions on aqueous subphases. These were prepared with ultrapure water supplied by a Millipore system with resistivity of 18.2 MΩ cm, with a KSV5000 Langmuir trough housed in a class 10 000 clean room. In some experiments, CdCl₂ (Carlo Erba) at a concentration of 4×10^{-4} M was added to the subphase, which also contained 5×10^{-5} M Na₂HCO₃ (Synth) to keep the pH at 6.0. Surface pressure and surface potential of the monolayer were measured using a Wilhelmy plate and a Kelvin probe, respectively, both provided by KSV. All experiments were conducted at room temperature, approximately 22 °C. Monolayer compression was carried out at a barrier speed of 10 mm min⁻¹. Stability tests were performed for the mixed films and pure Rupy and Rupic films maintaining the surface pressure at 15 mN m⁻¹, while the time evolution of the area per molecule was recorded. For the mixed films the area per molecule decreased only ca. 5% for a period of 7 h, indicating good film stability. In consecutive runs, reproducible results were obtained after the third run of compression–decompression cycles, when the films presumably reached a reasonable stability.

LB films were produced by transferring pure Rupy and Rupic and mixed monolayers onto ITO (indium–tin oxide)-coated glass (Asahi Glass Co., Japan), quartz, or silicon wafers (Aldrich). The typical dipping speed was 3 mm min⁻¹, with 30 min elapsing between the first and second layers, and 5 min for the subsequent layers when the substrate was out of the aqueous subphase. Y-type LB films were produced, keeping the surface pressure at 15 mN m⁻¹. The transfer ratios (TR) for the first 10 layers of the pure films was 0.9 for downstrokes and 1.2 for upstrokes. Upon further deposition the TR decreased to 0.5 for the remaining layers, in the upstrokes as well as in the downstrokes. For the mixed films TR varied from 0.96 to 0.98, i.e., effectively 1, for upstrokes as well as downstrokes for a larger number of layers (typically 41 layers were deposited).

The LB films on silicon wafers with 41 layers were characterized by FTIR spectroscopy using a BOMEM MICH-ELSON FT, MB 102, in the 4000–500 cm⁻¹ range and 4 cm⁻¹ resolution (20 scans min⁻¹). UV–vis absorption measurements were carried out in a HITACHI U-2001 spectrophotometer in the range between 350 and 800 nm, for the LB films deposited onto ITO (indium–tin oxide)-coated glass (Asahi Glass Co., Japan). LB films transferred onto ITO were characterized by X-ray diffraction using a Rigaku Rotaflex RU 200-B, with a tube voltage of 100 kV and tube current of 50 mA.

For the sake of comparison with the LB films, cast and spin-coated films of Rupy and Rupic were also obtained.

3. Results and Discussion

3.1. Monolayers at the Liquid–Air Interface. Langmuir films from neat Rupy or Rupic on pure water are not true monomolecular layers.^{4,5} Nonmonomolecular structures are formed as the surface pressure rises, and at the condensed state

the area per molecule is usually much lower than that required to accommodate a molecule in a monolayer structure. For example, the area extrapolated to zero pressure at the condensed region for the film was 31 Å² for Rupy and 28 Å² for Rupic. These values are lower than expected from theoretical calculations using the CPK model in the Hyperchem program, according to which Rupy and Rupic should occupy areas of ~140 Å². The low values of area per molecule are consistent with the shift in the surface pressure (π – A) isotherms toward lower areas during the initial successive compression–expansion cycles for the pure Ru complexes. Only after the third cycle was stability reached. This shift could be due to either loss of material to the subphase¹⁷ or molecular reorganization leading to nonmonomolecular structures. The stability reached in the third cycle points to the latter hypothesis as the most probable.

The question then arises as to whether monomolecular structures could be obtained in the mixed films with stearic acid. Figure 2 shows surface pressure isotherms for 1:3 Ru:SA, 1:1 Ru:SA, and 3:1 Ru:SA relative concentrations of Rupy or Rupic and stearic acid. The abscissa is given in terms of average area. The increase in area upon incorporation of the ruthenium complex demonstrates that its molecules are at the interface. However, the increase is still lower than should be expected if the ruthenium complexes formed monomolecular structures. Table 1 shows the extrapolated areas, which are again lower than required to accommodate the ruthenium complex in a monolayer. For the high Ru complex concentrations (1:1 and 3:1), the isotherms have a small plateau region, which was not seen in pure stearic acid or in the isotherms of pure Rupic and Rupy. This feature may be attributed either to a phase transition from an expanded liquid to a condensed state, or to the formation of nonmonomolecular structures. A plateau region was also observed in mixed films of [Ru(L)(4'-totpy)(H₂O)](ClO₄)₂ (L = (C₆H₅)₂AsCH₂CH₂As(C₆H₅)₂; 4'-totpy = 4'-(4-tolyl)-2,2':6',2''-terpyridine))¹⁸ complex with arachidic acid. It was attributed to some miscibility of the ruthenium complex with the fatty acid molecules at the liquid–air interface.¹⁸

The addition of stearic acid increased film stability considerably, with reproducible isotherms being obtained in successive compression–expansion cycles. The incorporation of ruthenium complex causes the stearic acid monolayer to become more expanded and more compressible, even when compared with those of the pure ruthenium complexes.

The expected area for a mixed monolayer (A_{12}) based on a simple ideal behavior for immiscible components¹⁸ is $A_{12} = N_1A_1 + N_2A_2$, where A_1 is the area occupied by each stearic acid molecule (assumed to be 20 Å²), A_2 is the area per molecule for the Rupic complex (taken as 148 Å² from CPK model), and N_1 and N_2 are the relative concentrations of the two components. This linear dependence of the area per molecule should also be observed if the components mix at the molecular level with no specific interaction. Figure 3 shows clearly that a linear relationship does not hold for mixed films of Rupic with stearic acid. The same applies to the mixtures of Rupy and stearic acid (results not shown). For a smaller amount of complex (1:3 Ru:SA), the measured area per molecule approximates that corresponding to a true monomolecular layer, which should be expected due to the monolayer-forming ability of stearic acid. Subsidiary experiments indicated that films with this relative concentration are more stable than those with the other mixing ratios.

Rupic and Rupy behave differently from a similar biphosphine ruthenium complex, [Ru(dppe)(4'-totpy)(H₂O)](ClO₄)₂ (dppe = PPh₂(CH₂)₂PPh₂).¹⁹ For mixed films with palmitic acid, the

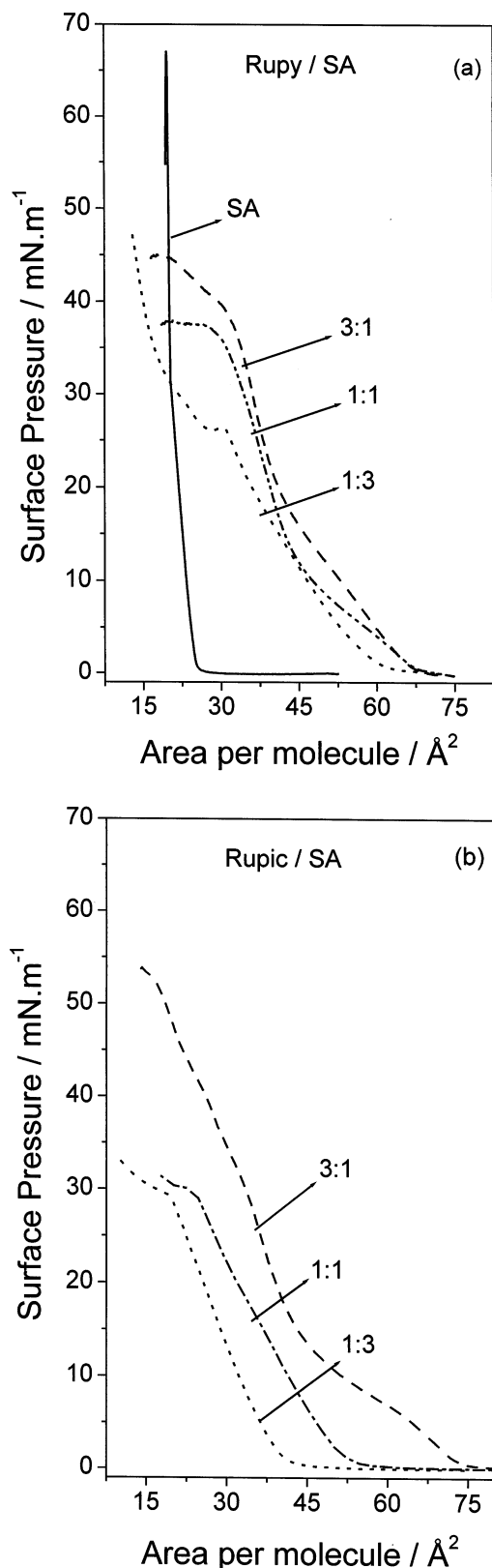


Figure 2. Surface pressure–area isotherms for pure stearic acid and for Rupy/SA mixtures (1:3, 1:1, and 3:1) on pure water subphases (a). Surface pressure–area isotherms for Rupic/SA mixtures (1:3, 1:1 and 3:1) on pure water subphases (b). The area per molecule was calculated as an average for the mixed films.

estimated area occupied by each ruthenium complex molecule was close to zero, as the average area per molecule was only 21 Å². This is practically the value for pure palmitic acid.

TABLE 1: Extrapolated Area and Maximum Surface Potential for Langmuir Films of Pure Rupy, Rupic, and Stearic Acid and Mixed Films (Subphase: H₂O)

| monolayer | area (Å ²) | max potential (V) | monolayer | area (Å ²) | max potential (V) |
|-------------|------------------------|-------------------|--------------|------------------------|-------------------|
| SA | 20 | 0.16 | SA | 28 | 0.89 |
| Rupy | 31 | 0.89 | Rupic:SA 1:3 | 41 | 0.52 |
| Rupy:SA 1:3 | 32 | 0.48 | Rupic:SA 1:1 | 53 | 0.65 |
| Rupy:SA 1:1 | 56 | 0.62 | Rupic:SA 3:1 | 55 | 0.69 |
| Rupy:SA 3:1 | 52 | 0.82 | | | |

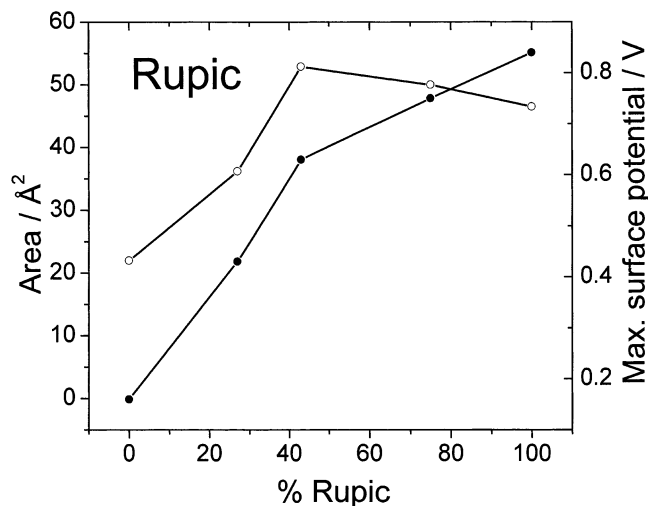


Figure 3. Maximum surface potential (solid circles) and extrapolated area per molecule (open circles) vs mole percent Rupic in the mixed monolayers. The lines are drawn only to guide the eyes.

Therefore, the ruthenium complex was probably located below the palmitic acid molecules and did not contribute to the measured area. For Rupic and Rupy, on the other hand, the interaction results from the complexation with the stearic acid molecules (see below), which is confirmed by FTIR data on Langmuir–Blodgett (LB) films to be shown later.

We also characterized the mixed films using the surface potential technique. The measured surface potential is proportional to the normal component of the total dipole moment of the molecular groups in the Langmuir film. Estimation of these dipole moments for molecules such as Rupic and Rupy is not possible because one cannot determine the precise orientation of the molecules at the air–water interface. Therefore, only qualitative information can be obtained from these measurements. For instance, the surface potential for the mixed films with three molecules of Rupic for one molecule of stearic acid (Ru:SA = 3:1) in Figure 4 is nonzero even at large areas per molecule, suggesting that large aggregates are formed immediately after spreading. Also, incorporation of the ruthenium complexes increases the surface potential of the film. The values for the maximum surface potential are shown in Table 1, which also lists results for Rupy that are similar in nature to the results for Rupic. Figure 3 shows that the increase in potential with the amount of Rupic is not linear, even though departure from linearity is not as clear as it is for the area per molecule. This again points to interaction between the ruthenium complex and stearic acid. A decrease in potential is observed as the film becomes condensed for the 1:3 Rupic:stearic acid ratio (Figure 4). Decreases such as this usually indicate considerable molecular reorientation, but the data do not suffice to further elaborate on this hypothesis.

In summary, the surface pressure and surface potential results indicated that there is interaction at the molecular level between

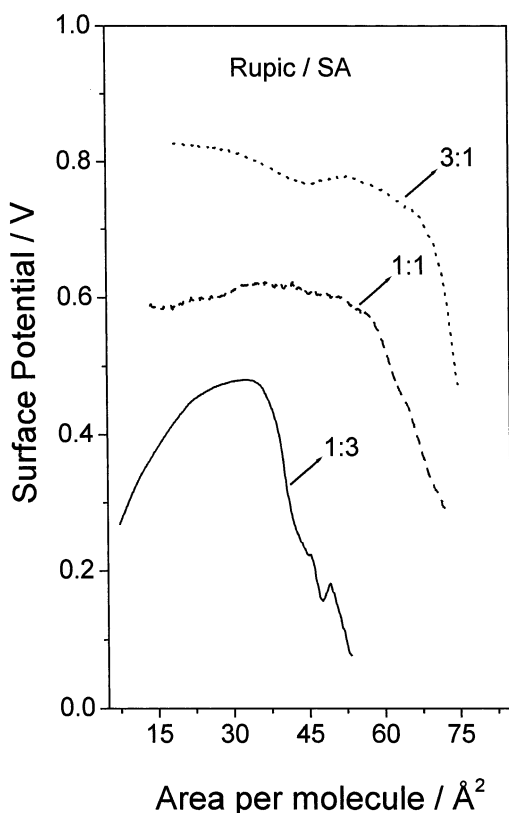


Figure 4. Surface potential–area isotherms for mixed Rupic/SA films on ultrapure water subphases. The area per molecule was calculated as an average.

TABLE 2: Extrapolated Area and Maximum Surface Potential for Langmuir Films of Pure Rupy, Rupic, and Stearic Acid and Mixed Films (Subphase: CdCl_2 -Containing Subphase (pH 6.0))

| monolayer | area (\AA^2) | max potential (V) | monolayer | area (\AA^2) | max potential (V) |
|-------------|----------------------------|----------------------|--------------|----------------------------|----------------------|
| CdSt | 22 | 0.17 | CdSt | 36 | 0.84 |
| Rupy | 45 | 0.92 | Rupic | 36 | 0.43 |
| Rupy:SA 1:3 | 39 | 0.52 | Rupic:SA 1:3 | 36 | 0.43 |
| Rupy:SA 1:1 | 56 | 0.60 | Rupic:SA 1:1 | 53 | 0.63 |
| Rupy:SA 3:1 | 51 | 0.82 | Rupic:SA 3:1 | 50 | 0.75 |

stearic acid and the ruthenium complex. One may postulate that interaction is due to complexation of stearic acid, which is partially charged, and the ruthenium complex, even though the latter is neutral. Indeed, complexation is confirmed in results for deposited LB films (see section 3.2). To further investigate complexation, one may employ a cadmium-containing subphase at a pH under which stearic acid is completely ionized. We used such experimental conditions, with an aqueous subphase containing CdCl_2 and Na_2HCO_3 leading to pH 6. Overall, the isotherms for the mixed films of stearic acid (or cadmium stearate, CdSt) and Rupic (or Rupy) were similar to those of the mixed films on pure water. The area per molecule was slightly larger for the films on the cadmium-containing subphases. These values are shown in Table 2. The nonlinear change in area per molecule and in the surface potential with increasing concentration of the components is, again, characteristic of interacting components. This nonlinear behavior contrasts with data for mixed films of stearic acid and several compounds, such as lignins,¹³ polyaniline,²⁰ and 16-mer polyaniline.²¹ In all these cases, a linear increase was found to be due to nonmiscible components, as the separate domains of

stearic acid (or cadmium stearate) could be observed in X-ray diffractograms of transferred LB films.

3.2. Langmuir-Blodgett (LB) Films. LB films could be deposited from pure Rupic or Rupy, or from mixtures with stearic acid or cadmium stearate. Some properties of Rupic and Rupy films have been discussed in refs 4 and 5, respectively. Two essential features from these studies were the marked influence of the layer-by-layer nature of the LB films in the final film properties and the interaction at the molecular level between ruthenium complex and polyaniline (Pani) in mixed films. For example, electroactivity was observed in pure Rupic and mixed LB films with stearic acid, but not in cast films. In these latter films the absence of the electroactivity was ascribed to the lack of order of the metallic complex.⁴ The interaction between Rupy and Pani, on the other hand, made the mixed films exhibit more stable electrical properties than pure Pani films.⁵ As mentioned in section 2, the transferability of LB films was improved with the mixed film approach when the ruthenium complex was co-spread with stearic acid. Y-type LB films could be transferred with a transfer ratio of ca. 1 for several relative concentrations of Rupic or Rupy and stearic acid, e.g. 1:3, 1:1, and 3:1. UV–vis results (not shown) indicated that a constant amount of material was transferred after each dipping cycle. For LB films from pure Rupic or Rupy, a linear increase was observed up to 25 layers or so, after which a smaller amount of material was transferred in each cycle.

In the present work we concentrated on the spectroscopic characterization of LB films, to probe the interaction between the ruthenium complex and stearic acid. Figure 5a shows FTIR spectra for a spin-coated film from Rupy and from 41-layer LB films deposited onto Si substrates. The LB films were made from pure Rupy and 1:1 mixtures of Rupy and stearic acid transferred from a pure water subphase and from a cadmium-containing subphase (i.e., Rupy:CdSt film). The main bands of the spectra are tentatively attributed in Table 3. No information can be obtained in the 200–500 cm^{-1} range due to the influence of the Si substrate. The spectrum for the spin-coated film is essentially the same as that from Rupy in bulk form, in KBr or CsI pellets.¹⁶ When the spin-coated film includes stearic acid, the spectrum is the superposition of the bands of Rupy and stearic acid, which indicates no interaction between the components. For the sake of clarity only the spectrum for the Rupy/SA (1:1) LB film, transferred from a pure water subphase, is shown in Figure 5b in the range from 2700 to 3200 cm^{-1} . The spectra of other films show the same bands. Those at 2920 and 2850 cm^{-1} are assigned, respectively, to methyl and methylene groups of stearic acid¹ and coincide with the $\nu(\text{C}-\text{H})$ bands for the aromatic and aliphatic groups of the dppb ligand.¹⁶ The carboxylate group contributes with a broad band around 1584 cm^{-1} for the Rupy:SA film and 1543 cm^{-1} for the Rupy:CdSt film (Figure 5a). Upon comparison with the spectrum of pure stearic acid or cadmium stearate films,¹ one notes that this band is broader for the mixed films with Rupy, which points to some disorder of the carboxylate group or interaction with other groups.

Complexation of the carboxylate group was inferred because there was no significant band at 1700 cm^{-1} . This applies not only to the mixed films transferred from the cadmium-containing subphase but also to those transferred from an ultrapure water subphase. In the former case, complexation may have occurred with the cadmium ions or with Ru^{3+} . Indeed, the shift in the carboxylate band for the Rupy:CdSt film is probably due to a competition between Ru^{3+} and Cd^{2+} for the ionized stearic acid headgroup. It may be postulated that for the Rupy–stearic acid

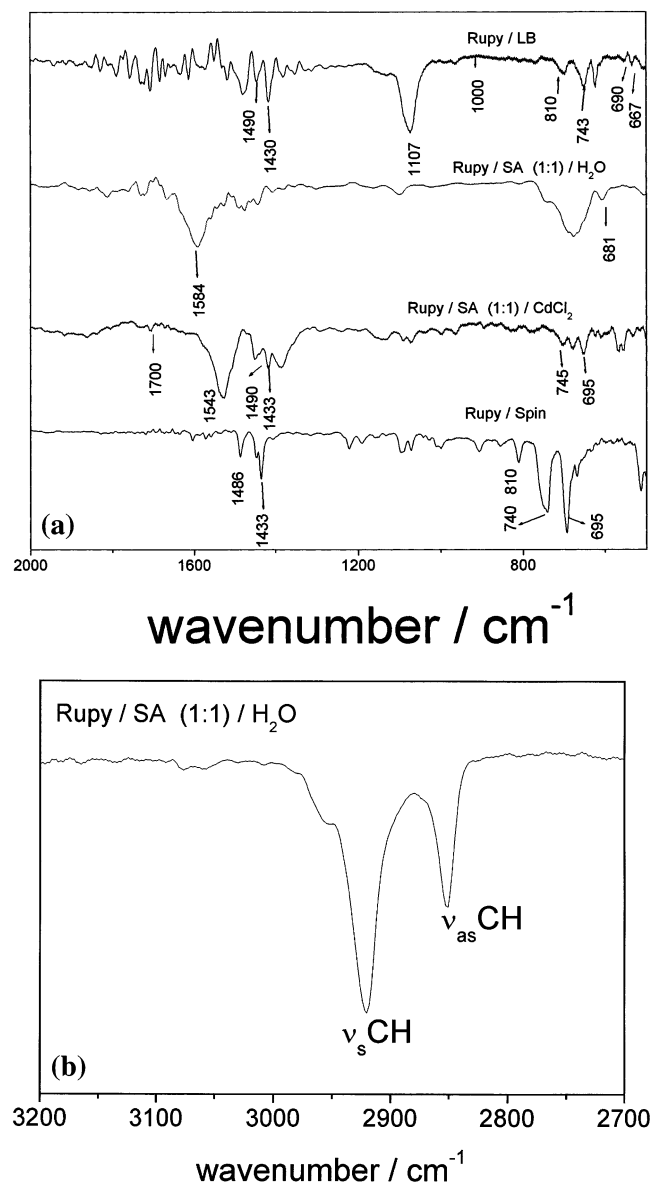


Figure 5. (a) FTIR spectra of a spin-coated neat Rupy film and from three LB films: pure Rupy and from Rupy/SA (1:1) mixtures transferred from a pure water subphase and from a CdCl₂-containing subphase. The LB films had 41 layers deposited on Si. (b) FTIR spectrum for the 2700–3200 cm⁻¹ range for a 41-layer LB film from Rupy/SA (1:1) mixture, transferred from a pure water subphase onto a Si substrate.

complexation one of the chlorides was labilized in order to coordinate with the ionized stearic acid, thus keeping the Ru(III) oxidation state of the film. The film is therefore neutral. To our knowledge, this is the first example of complexation between ionized fatty acids and neutral metallic complexes. In ref 19, complexation occurred in palmitic acid but for the charged biphosphine ruthenium complex [Ru(dppe)(4'-totpy)-(H₂O)](ClO₄)₂,¹⁹ in which palmitic acid replaced the ClO₄ counterion that was in the solvation layer of the ruthenium.

It should be emphasized that the discussion presented above for the FTIR spectra of Rupy also applies to Rupic, including complexation with stearic acid. Owing to the similarity of the results, we omitted the data for Rupic.

The most striking effect from the layer-by-layer nature of the LB films appeared in the electronic spectra. Figure 6 shows the data for Rupy in various forms: in chloroform solution (a), as cast films (b), or in neat (d) or mixed LB films (c, e, f, g). Cast or spin-coated films of mixtures of Rupy and stearic

TABLE 3: Assignments of Various Bands Observed in the FTIR Spectra of Films

| LB film | | | | assignment |
|-------------|----------------------------------|------------------------------------|-----------------------|--|
| Rupy (pure) | Rupy:SA (H ₂ O) (1:1) | Rupy:SA (CdCl ₂) (1:1) | spin-coat Rupy (pure) | |
| 2926 | 2922 | 2924 | 2924 | $\nu(\text{C-H})$ asym |
| 2869 | 2852 | 2847 | 2861 | $\nu(\text{C-H})$ sym |
| | | 1700 | | $\nu(\text{C=O})$ |
| | 1541 | 1543 | | $\nu(\text{COO})$ |
| 1490 | 1490 | | 1486 | $\nu(\text{P-C})$ |
| 1430 | 1433 | 1433 | 1433 | $\nu(\text{P-C})$; $\nu(\text{C-H})$ ring |
| 1107 | 1100 | 1108 | | $\nu(\text{P-C})$ |
| | | 1098 | 1092 | $\nu(\text{P-C})$ |
| 1000 | | 1005 | 1004 | $\nu(\text{P-C})$ |
| 810 | | | 810 | $\delta(\text{C-H})$ ring |
| 743 | | 743 | 745 | $\gamma(\text{C-H})$ ring |
| 690 | 680 | 695 | 695 | $\gamma(\text{C-H})$ |
| 510 | | 515 | 513 | $\nu(\text{P-C})$; $\nu(\text{Ru-P})$ |

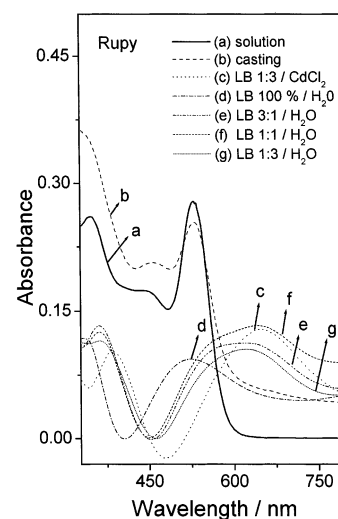


Figure 6. Electronic absorption spectra recorded for Rupy in various forms: in chloroform solution (a), as neat cast film (b), in neat LB films (d), or in mixed LB films (c, e, f, g).

acid lead to spectra that are identical to those of cast films from pure Rupy. Rupy data were omitted due to the observed similarity to those for Rupy. The spectra for solution and the cast films are similar, with main bands at 350, 445, and 527 nm. These bands were attributed to the charge transfer between metal and ligands.¹⁶ For the pure Rupy LB film, the two bands at larger wavelengths cannot be distinguished, and a broad band centered at 545 nm appears. This imparts a reddish color to the film, whereas in solution or in the cast film the color was bright red. An even larger effect in color change occurs for the mixed films. Curves c–g indicate that a new band appears at ca. 650 nm for the several relative concentrations of Rupy and stearic acid. The differences in the vibrational spectra are also reflected in color change, from red in solution to bluish green in the mixed LB film. This change in color was not observed in cast films of Rupy mixed with stearic acid, or in chloroform solution containing the two components. In subsidiary experiments we changed the solvent (acetonitrile, nitromethane, and dichloromethane) but the solution was still red, ruling out the possibility of solvatochromism. Therefore, the change in color must be associated with an order-induced effect in the LB film or with the exposure of the ruthenium complex to the water subphase for preparing the Langmuir and LB films. When LB Rupy films were transferred from cadmium-containing subphase (curve c), the same change in color was observed. LB films

from Rupy also displayed similar changes in electronic spectra and in color.

Further confirmation of the molecular-level interaction between the ruthenium complex and stearic acid (or cadmium stearate) was obtained in X-ray diffraction data for mixed LB films. In previous studies with mixed films of cadmium stearate and polymers^{12,22,23} or lignin,²⁴ Bragg peaks were observed with a bilayer distance of ca. 50 Å, which is characteristic of a bilayer of cadmium stearate. This was interpreted as due to the separation of CdSt domains from the domains of the other component. We have obtained diffractograms in the 2θ range up to 50° for mixed LB films of Rupy or Rupic and CdSt and no Bragg peaks could be identified. Therefore, the interaction at the molecular level prevents CdSt domains from being formed. Diffractograms of LB films from pure Rupy or Rupic do not exhibit Bragg peaks, either, which indicates that these films do not form crystalline structures with long-range order.

4. Conclusions

Interaction at the molecular level was inferred to occur between biphosphine ruthenium complexes and stearic acid, both in Langmuir films and in LB films. In the Langmuir films, the area per molecule and the surface potential did not vary linearly with the relative concentration of the acid, which points to molecular-level interaction between the compounds. In the LB films, interaction was observed in three instances: (i) evidence of complexation in the FTIR spectra between the ruthenium complexes and stearic acid, even though the complexes were neutral; (ii) changes in the electronic absorption spectra of the mixed films, which are also manifested as a color change that is only observed in LB films; (iii) absence of Bragg peaks in X-ray diffractograms, because separate domains of CdSt are not formed. It remains to be explained whether the change in color already occurs at the air–water interface. Experiments are underway to test this possibility.

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