Formation of Mosaic Monolayer and Uniformly Mixed Monolayer of the Mixture of Copper(II) and Nickel(II) Complexes Coordinated with Butyl-Substituted Salen

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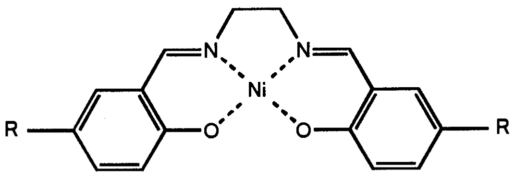
Two methods have been employed to form different types of monolayers from the mixture of copper(II) and nickel(II) complexes at air-water interface. When the complexes are mixed up before they are put onto the water surface, the π-A isotherm measurement revealed that a uniformly mixed monolayer was formed. On the other hand, when the complexes are dissolved individually and put onto the water surface successively, a mosaic monolayer of the component complexes with independent domains was formed. The domains of the copper(II) complex in the mosaic monolayer could be selectively compressed.

The metal complexes of bis(salicylidene)ethylenediaminato ion, usually abbreviated as salen, exhibit a variety of aggregates in crystal, and the aggregating nature of the salen complex is known as highly dependent on the central metal ions. In the crystalline phase, the nickel(II) complex forms no apparent aggregates,[1] but the cobalt(II) complex forms dimers with metal-metal interaction.[2] The copper(II) complex also forms dimers but with metal-oxygen interaction.[3] These differences indicate that the aggregating nature of the salen complexes is dependent on the nature of the central metal ions.

Previously, we have reported that the nickel(II) complexes **1** of alkyl-substituted disalicylideneethylenediamine, usually abbreviated as salen, formed two kinds of smectic liquid crystalline phases upon melting.[4] The complexes were also found to exist in the form of dimers in the crystalline state by X-ray crystallographic analysis performed on the butyl-substituted analogue.[5] In the dimer, the π-conjugated systems of the salen moieties were stacked and also the CH-π interactions between CH of butyl side chains and π-conjugated system were present. The monolayer images of the butyl-substituted complex observed by the scanning tunnelling microscopy (STM) measurement, revealed that the complex molecules were also in the form of dimers in the monolayer state.[6] Moreover, the structural data of the dimer were almost in accord with those in the crystalline state, both in displacement and spacing. This fact suggests that the CH-π interactions are also present in the monolayer.



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The copper(II) analogue, recently synthesized, was found to form monolayer similarly to the corresponding nickel(II) complexes with two monolayer states (Figure 1). The monolayer states with large limiting area and that with small compressed limiting area were named the expanded phase and the condensed phase, respectively.[6] Although the limiting area of the condensed phase was almost identical to that of the nickel(II) analogue, the limiting area of the expanded phase was somehow decreased by 20%. Since the sizes of the copper(II) complex and the nickel(II) complex are almost identical, this large difference should be caused by the difference in the aggregating structure in the expanded phases. The reason why the limiting areas for the nickel(II) complex and copper(II) complex differ by about 20% is not clarified yet, but the presence of CH-π interaction in the monolayer of nickel(II) is a factor that increases the limiting area, and thus is a good candidate for that reason. The pressure at which the phase transition from expanded phase to condensed phase also decreased drastically by 60%, indicating the weakness of the monolayer structure of copper(II) complex. This difference should be caused by the difference in the intermolecular interactions inside the monolayer. Such a difference has also been observed in the case of [*N*,*N*'-bis(5-(1,1-dimethylpropyl)salicylidene)ethylenediaminato]nickel(II)[7] in which the intermolecular interaction is weakened by the steric effect of the methyl groups substituted at the α-position of the alkyl side chains.

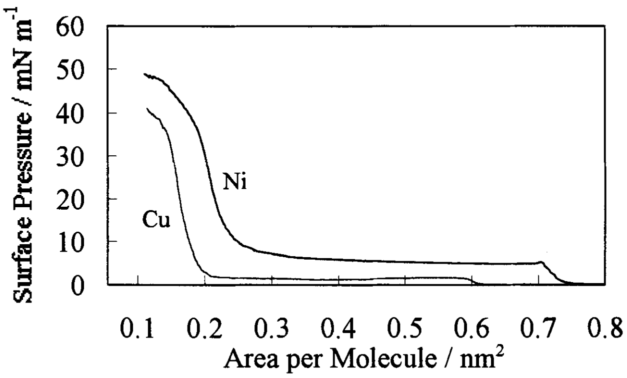

Figure 1. π-A Isotherms of the Ni(II) and Cu(II) complexes.

When these two complexes were mixed to form a monolayer, two different types of monolayers namely I and II could be made independently. Monolayers were formed on the water surface according to the following procedures. The 1.3 mmol dm^{-3} chloroform solution of the complex(es) was put onto the surface (940 cm^2) of distilled water prepared by Autostill WG-260 of Yamato Scientific Co. using a micro syringe at 25°C. Then the chloroform was allowed to evaporate for about 30 min. A platinum plate was used to measure the surface pressure π and the area (A) being narrowed at a rate of 7 cm^{2}min^{-1}.

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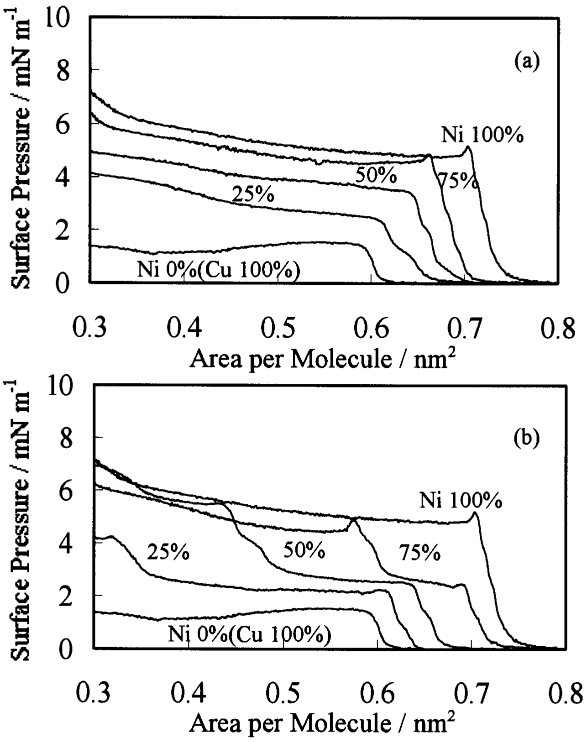

Figure 2. π-A Isotherms of (a) I, the uniformly mixed monolayers and (b) II, the mosaic monolayers. Percentages are that of the nickel complex.

The complexes used were nickel(II) and copper(II) complexes of *N*,*N*'-bis(5-butylsalicylidene)ethylenediaminato ion (abbreviated as C4-salen) synthesized according to the reported method. The π-A isotherm was obtained using type HBM-AP of Kyowa Interface Science Co. and recorded by personal computer NEC PC-9821cb. Two types of monolayers, the monolayer I and the monolayer II, were formed at a water-air interface. The monolayer I was obtained using independently dissolved chloroform solutions of the copper(II) and nickel(II) complexes and placing them successively on the air-water interface by a micro-syringe. The monolayer II was obtained by the similar procedure but by using premixed chloroform solution of the complexes instead.

In Figure 2 are shown the π-A isotherm of the monolayer I (a) and that of the monolayer II (b) of the mixture of nickel(II) and copper(II) complexes coordinated with butyl-substituted salen. The percentages in the Figures 2(a) and (b) represent the molar ratio of nickel(II) complex, and the residue consequently represents that of the copper(II) analogue. Two monolayer states can be clearly distinguished by their π-A isotherm curves. The π-A isotherm of the mixture in the monolayer I exhibited only one pressure increase due to the formation of expanded phase, while that in the monolayer II exhibited two pressure increases. Since the phase transitions in the monolayer II occur at almost the same pressures as those of the nickel(II) and copper(II) complexes, it is clear that the nickel(II) and copper(II) complexes are not mixed up but they form independent molecular domains in the mosaic manner. This can be confirmed by the fact that the difference in the values of area per molecule for the two pressure increases changes proportionally to the percentage of the copper(II) complex. Thus the monolayer II is named the mosaic monolayer, and the monolayer I, in which the complexes are mixed up uniformly, is named the uniformly mixed monolayer to distinguish the two. Figure 3 schematically illustrates the changes brought about by the compression of the mosaic monolayer. The darkness of the domain indicates the density of the complex. The copper(II) domain should be selectively compressed at the relatively flat region where the narrowing of the area from 0.63 to 0.48 nm^2 induces phase transition only in the copper(II) domain.

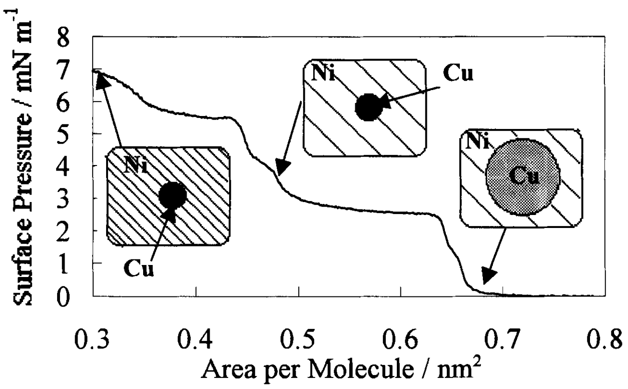

Figure 3. Schematic illustration of the changes in the mosaic monolayer (Ni 50%) induced by compression.

Note that the limiting areas for the uniformly mixed monolayer, shown in Figure 2(a), tend to decrease almost proportionally to the percentages of nickel(II) complex. The pressures of phase transition for the uniformly mixed monolayer also decreased, but took slightly larger value than the averaged value. These two complexes only differ in the central metal ion, and thus it is natural that their mixture forms uniformly mixed monolayer. The mosaic monolayer was realized because the formation of monolayer state is so rapid that they stop moving before they are mixed up due to the hardness of the monolayer. The hardness of the monolayer can be confirmed from the fact that the π-A isotherms of these complexes exhibit bumps after the phase transition occur.

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