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Monolayers and Built-up Films of *N,N'*-Disubstituted Dithiooxamide Cu(II) Coordination Compounds*

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N,N'-Disubstituted dithiooxamide-Cu(II) as compound semiconductors prepared by the usual method have been liable to be an isomeric mixture of coordination polymers. Syntheses of the stereospecific coordination polymers were attempted by an interfacial technique. The dithiooxamides with two hydrophobic substituents, R's, on nitrogen atoms of a ligand molecule could be spread on a water surface to form the monomolecular film, where its possible structure is *cis* isomers of the ligands. Some coordination compounds, *i.e.* the stereospecific coordination polymers, between the *cis* isomers and Cu^{2+} ions were found to be produced at the air-water interface by employing the substrate solution containing Cu^{2+} ions. This was established by the surface pressure *vs.* area measurements for their ligand molecules with $C_6H_5CH_2$–, C_6H_{11}–, $C_{12}H_{25}$–, and $C_{12}H_{25}OCOCH_2$– as hydrophobic substituents, and by the effects of various spreading solvents, pH in substrate solutions and temperatures on their monolayers. Furthermore, built-up films of these polymers were examined for thickness.

N,N'-Disubstituted dithiooxamide–Cu(II) complex (R-DTOA-Cu) have been studied as a series of organic or metal-organic semiconductors.1) In our study the coordination polymers were prepared by "bulk method," that is, a simple mixing of the solutions of the both components. From their chemical compositions and the properties, a two-dimensional polymeric structure has been proposed for the compounds,2) although a linear chain structure had been proposed before.3) However, the preparation of R-DTOA–Cu by the "bulk method" might result in the isomeric mixtures called type A because of a rotational isomerism around the central carbon-carbon bond of the ligands themselves (Fig. 1a) and the coordination isomerism in the compounds as a whole (Fig. 2). Actually all of the black precipitates show a few diffused hallows for each compound in their X-ray diffraction patterns by the powder method.2). The discussions on electric, magnetic, and other properties, which are more or less related to the stereostructure of the molecules, would be restricted because of the isomeric irregularity.4)

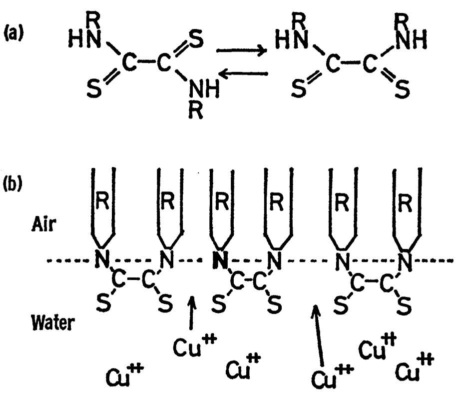

Fig. 1a. Expected rotational isomerism of the ligands.
1b. A schematic mechanism of the stereospecific synthesis of the type B compounds.

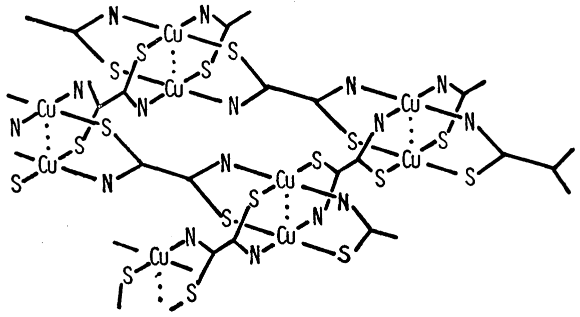

Fig. 2. Non-stereospecific two-dimensional net-work model with dimer structures of copper acetate type. For simplicity, substituents on nitrogen atoms are omitted.

For the solution of the ambiguity, the stereospecific synthesis of the polymers has been attempted by the "monolayer method" in which the ligands with the two hydrophobic substituents on the nitrogen atoms are spread on an aqueous subphase containing cupric ions (Fig. 1b) and the resultant products are called type B. The reaction yields of the type B compounds of $C_6H_5CH_2$–, C_6H_{11}–, and $C_{12}H_{25}$–DTOA–Cu seem to be more or less qualitative.4),† On the other hand the coordination of a new ligand, dodecyl ester of $HOOCCH_2$-DTOA-H_2, with Cu^{2+} ions at the air/water interface seems to be quantitative as shown in this study, and the monomolecular film is stable. As a result, the molecular structures of the type B compounds are confirmed, and some properties of the coming built-up films might be interpreted in relation to this molecular structure.

Experimental

Materials. *N,N'*-Disubstituted dithiooxamides, RNH–C(S)–C(S)–NHR, in which the R's were $C_6H_5CH_2$– (benzyl), C_6H_{11}– (cyclohexyl), and $C_{12}H_{25}$–(dodecyl), were from the

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† The preliminary study of diffraction patterns by the X-ray powder method and the presumption about the crystallinity mentioned in the previous paper (Ref. 4, pp. 91, 95) need supplemental experiments and more carefull consideration on the data.

Mallinckrodt Chemical Works, and was recrystallized from ethanol. Dodecyl ester of *N,N'*-carboxymethyl dithiooxamide, $C_{12}H_{25}OC(O)CH_2NHC(S)C(S)NHCH_2C(O)OC_{12}H_{25}$, was prepared from dodecyl alcohol and *N,N'*-bis(carboxymethyl)-dithiooxamide in the presence of a acid catalyst, H_2SO_4. The crude ester was recrystallized from acetone, mp 101 °C (uncorrected). Cupric sulfate (Special Grade Reagent, Wako Pure Chemical Industries, Ltd.) was heated for 2 hr at 350 °C in a furnace to diminish the surface active contaminations. The organic solvents (Special Grade, Wako P.C.I., Ltd.) were distilled twice. Water used for the subphase was distilled in a copper distillatory first and in a glass vessel next. Solid substrates, glass and quartz plates, were cleaned by a ultrasonic method with help of detergent followed by a treatment with hot cleaning solution ($Na_2Cr_2O_7$ in concd H_2SO_4). For the purpose of uniform deposition of the complex monolayer, each solid substrate was coated with three monolayers of Fe-stearate under the surface pressure of 29 dyn/cm.

Procedure. About 2 mg of the ligand was dissolved in 10 ml of the binary mixed solvents composed of ethanol, propanol, benzene, or hexane as shown in Figs. 3—6. The solution was spread from an Alfa micrometersyringe on water or aqueous solution in a conventional Langmuir trough ($60\times 13.5\times 1$ cm^3). The surface pressure (π) was measured by a automatic recording systems as a function of the surface area (A) using the hanging plate method.[5)] Unless otherwise specified, the measurements were carried out at a room temperature (15—25 °C). In examining the temperature effects on complex monolayer, the temperature of the subphase was regulated at the selected values in the range of 20 to 5 °C by thermoelectric modules attached at the bottom of the trough.

Complex monolayers were transferred onto a solid substrate by the Langmuir-Blodgett method as follows. The Langmuir trough was divided into three sections for the "transfer method."[6)] The ligand solution was spread on an aqueous cupric solution in the first section and was allowed to stand for 30—60 min for the complete coordination reaction. The obtained complex monolayer was transferred to the water surface in the second section for washing the non-reacted Cu^{2+} ions adsorbed beneath the complex monolayer. Furthermore the monolayer was transferred to the third section filled with pure water, where the built-up procedure was carried out. It was made by an automatic equipment with a certain speed. During the procedure, the surface pressure of monolayer was kept constant by the piston oil. The pressure of piston oil was adjusted by changing the mixing ratio of ethylmyristate and liquid paraffin. The conditions for the preparation are shown in Table 1.

TABLE 1. CONDITIONS OF THE PREPARATION OF THE BUILT-UP FILMS OF R-DTOA-Cu

R	Spreading solvent	Spreading pressure (dyn/cm)
C_6H_{11}-	benzene : ethanol = 1 : 4	15
$C_6H_5CH_2$-	benzene : ethanol : hexane = 1 : 4 : 5	19
$C_{12}H_{25}$-	benzene : ethanol = 1 : 4	15
$C_{12}H_{25}OCOCH_2$-	benzene : hexane = 2 : 3	19

Results and Discussion

Monolayer. The spread monolayers of the ligands or the complexes on an aqueous subphase were studied in order to find the structure of the molecule at the interface and the optimum conditions for the preparation of built-up films. The mechanisms of spreading of the ligand and of the coordination reactions at an air/water interface are presumed as follows. The molecules of dithiooxamides having both hydrophilic and lipophilic parts would be oriented at the surface by surface free energy, forming a monolayer. Due to internal rotation around the central carbon-carbon bond of the ligand molecule the *trans*-form, which is more stable in crystal and probably in solution,[7)] is isomerized to the *cis*-form.

Equilibrium between the *trans*- and the *cis*-form of a ligand molecule at an air/water interface was studied as a first approximation by an equation, $-RT\ln([cis]/[trans])=-RT\ln K=\Delta F°=\Delta F_1+\Delta F_2$, where K denotes the equilibrium constant; $\Delta F°=F°(cis)-F°(trans)$, standard free-energy change in the reaction concerned; ΔF_1, the free energy change originated from an internal rotation of the isolated molecules; ΔF_2, that originated from the transfer of a hydrophobic substituent R from the water phase to the air phase. As an example, in case of $R=C_{12}H_{25}$–, the ΔF_1 was evaluated to be $+1.5$ kcal/mol by the measurement of the temperature variation of absorption intensities in an infrared region.[8)] The ΔF_2 per $-CH_2-$ group have been estimated to be $-(0.8—0.9)$ kcal/mol in a linear hydrocarbon chain, therefore, $\Delta F_2=-(0.8—0.9)\times 12=-10$ kcal/mol.[9)] Then the $\Delta F°$ is $-(8—9)$ kcal/mol, and $K=[cis]/[trans]$ at the interface is greater than 10^5 approximately. Also in the case of ligands with other hydrophobic substituents, $C_6H_5CH_2$–, C_6H_{11}–, and $C_{12}H_{25}OCOCH_2$–, analogous results are expected. In conclusion virtually all the ligand molecules are expected to take the *cis*-form at the air/water interface.[††]

Figure 3 shows the π-A isotherms obtained for the monolayers of ligands on distilled water at a room temperature (15—25 °C). The ligands having a pair of long hydrocarbon chains as the substituents, $C_{12}H_{25}$–

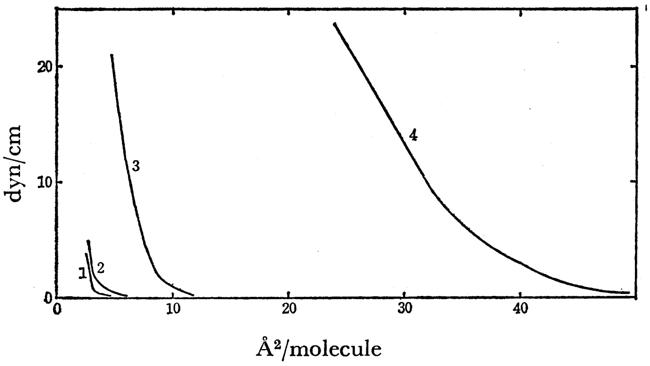

Fig. 3. Surface pressure *vs.* molecular area curves for R-DTOA-H_2 spread on pure water. Substituent, R, and spreading solvent with mixing ratio is as follows: 1) $C_6H_5CH_2$- (benzene 1, ethanol 4), 2) C_6H_{11}- (butanol 1, hexane 4), 3) $C_{12}H_{25}$- (ethanol 4, benzene 1), 4) $C_{12}H_{25}OCOCH_2$- (benzene 1, ethanol 1).

[††] The more extensive study on the *cis-trans* isomerization of the ligand molecules are now in progress, and will be published elsewhere.

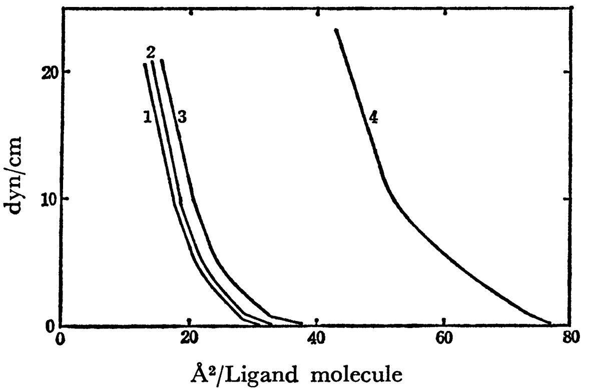

Fig. 4. Surface pressure *vs.* molecular area curves for R-DTOA-H_2 spread on 0.005 M $CuSO_4$ aqueous solution. Substituent, R, and spreading solvent with mixing ratio are as follows: 1) $C_{12}H_{25}$- (buthanol 1, hexane 4), 2) $C_6H_5CH_2$- (buthanol 1, hexane 4), 3) C_6H_{11}- (benzene 1, hexane 4), 4) $C_{12}H_{25}OCO$-CH_2- (benzene 2, hexane 3).

or $C_{12}H_{25}OCOCH_2$–DTOA–H_2, form monolayers on water, whereas the others, $C_6H_5CH_2$– and C_6H_{11}–DTOA–H_2, hardly spread over a water surface due to their poor hydrophobicity; the latters might be dissolved in the subphase owing to the fair solubilities of 0.14 and 0.12 g per 100 ml of water at 25 °C, respectively.[10] The limitting areas (A_0) estimated by extrapolation of the surface pressure to zero were 7 and 38 Å^2/molecule for $C_{12}H_{25}$– and $C_{12}H_{25}OCOCH_2$–DTOA–H_2, respectively. As the molecule has two hydrophobic substituents on both ends, A_0 values of the ligands should be larger than twice the value of the cross-section of a hydrocarbon linear chain, 20 Å^2/chain.[11] Data for the ester is reasonable but that for another is smaller than expected; the small A_0 can be attributed to pile-up of the ligand molecules on water due to the hydrophile-lipophile unbalance and/or the dissolution owing to the solubility of 0.06 g per 100 ml of water at 25 °C.[10]

Figure 4 shows the π-A isotherms of ligands spread on 5×10^{-3} M $CuSO_4$ aqueous solutions. In this case, $C_6H_5CH_2$– and C_6H_{11}–DTOA–H_2 exhibit detectable surface pressures due to a decrease in solubility with formation of a copper compound. The complexes of the type A of these two ligands are insoluble in water though the two ligands are slightly soluble in water as mentioned previously. The A_0 values were evaluated as 25, 22, 22, and 56 A^2/molecule for C_6H_{11}–, $C_6H_5CH_2$–, $C_{12}H_{25}$–, and $C_{12}H_{25}OCOCH_2$–DTOA–Cu, respectively. The former three values are smaller than that expected.

To obtain the conditions giving a reasonable limitting area, the concentration of Cu^{2+} ion, the compression speed, the spreading solvents, and the pH of the subphase were examined.[†††] As an example, the changes in the π-A isotherms of C_6H_{11}–DTOA–Cu complex are shown in Fig. 5a, b, c, d. In Fig. 5a, the π-A isotherms are shown as a function of Cu^{2+} ion concentration from 5×10^{-5} to 5×10^{-2} M. On the subphases of extreme cupric ion concentrations, 5×10^{-5} and 5×10^{-2} M, the results showed poor reproducibility and were found in ranges shown by the pairs of dashed and dotted lines. On the moderate concentrations, 5×10^{-4} and 5×10^{-3} M, reproducible π-A curves were obtained for both concentrations. The π-A curves observed with the various compression speeds are shown in Fig. 5b. The selected speeds were in a range of 0.33—2 cm/min (0.11—0.67 Å^2/molecule·min). The A_0 did not remarkably depend on the compression speed except for the highest one, 2 cm/min.

The mixtures of benzene–hexane, chloroform–hexane, 1-pentanol–heptane, 2-pentanol–heptane, or propanol–hexane were used as the spreading solvent, the mixing ratios were 1 : 4 by volume in most cases, and the results are shown in Fig. 5c. The character of the π-A curves was not changed essentially and only displacements of the π-A curves were observed. The effect of pH of subphases was examined by adjusting pH to the values from 2.9 to 10.2 with use of hydrochloric acid or sodium hydroxide. The results found on 5×10^{-3} M $CuSO_4$ aqueous solution are shown in Fig. 5d. In the acid region, the π-A relation was not remarkably affected by the pH, whereas in the alkali region A_0 was decreased with increasing pH. The effect of pH may be attributed to the decreasing concentrations of hydrated cupric

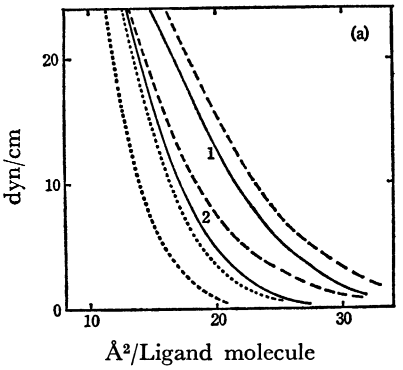

Fig. 5a. The effect of $CuSO_4$ concentration on π *vs.* A curve for C_6H_{11}-DTOA-Cu monolayer. Solid line 1) 5×10^{-3} M $CuSO_4$, Solid line 2) 5×10^{-4} M $CuSO_4$, Dotted lines) 5×10^{-5} M $CuSO_4$, Dashed lines) 5×10^{-2} M $CuSO_4$. Spreading solvent: benzene 1, hexane 4.

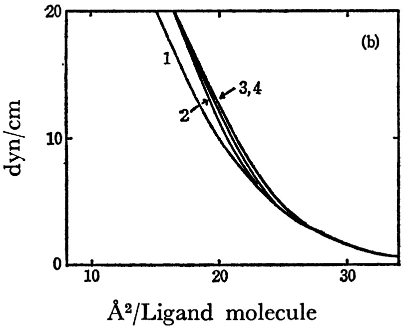

Fig. 5b. π *vs.* A curves with various compression speeds on a unit of Å^2/molecule·min: 1) 0.67, 2) 0.33, 3) 0.22, 4) 0.11. The film substance is C_6H_{11}-DTOA-Cu on 5×10^{-3} M $CuSO_4$ aq. Spreading solvent: benzene 1, hexane 4.

[†††] This experiment was mainly operated by Mr. Watari.

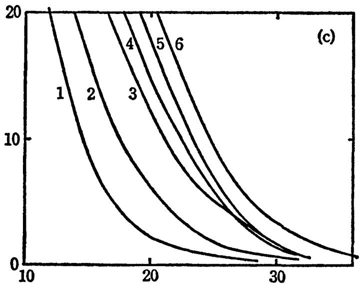

Fig. 5c. The effect of spreading solvents on π *vs.* A relation for C_6H_{11}-DTOA-Cu on 5×10^{-3} M $CuSO_4$ aq. The components and the mixing ratios: 1) benzene and hexane, 1 : 1, 2) chloroform and hexane, 1 : 1, 3) benzene and hexane, 1 : 4, 4) 1-pentanol and heptane, 1 : 4, 5) 2-pentanol and heptane, 1 : 4, 6) propanol and hexane, 1 : 4.

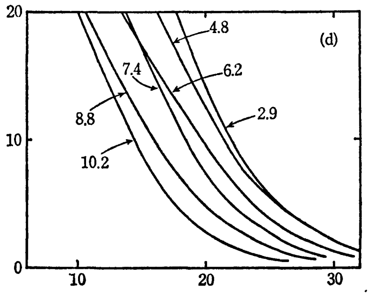

Fig. 5d. The effect of pH of the subphase on π *vs.* A for C_6H_{11}-DTOA-Cu on 5×10^{-3} M $CuSO_4$. pH of the subphases are indicated in the figure. Spreading solvent: benzene 1, hexane 4.

ions, $Cu(H_2O)_{4-6}^{2+}$, as Stickland discussed.[12]

The presented results so far for the monolayer of C_6H_{11}-DTOA-Cu indicate that the limitting area was rather small, in the range of 15 to 29 Å²/molecule. Even 30 Å²/molecule is still smaller than that expected for two hydrophobic substituents on the ligand molecule in the *cis*-form. This phenomenon could be caused from the dissolution of unreacting ligand molecules into water or the stacking of the copper complex which might be too hydrophobic to form a monomolecular film. A similar reasoning may be applicable to the monolayers of $C_6H_5CH_2$– and $C_{12}H_{25}$–DTOA–Cu complexes. The A_0's for $C_{12}H_{25}OCOCH_2$–DTOA–H_2 on pure water and on the cupric aqueous solution, 38 and 56 Å²/molecule, respectively, were reproducible, and the former is reasonably related to twice the limitting area of single chain fatty acids, therefore the quantitative formation of monolayer of the ester ligand in the *cis*-form was confirmed.

The effect of temperature on the π-A curves of $C_{12}H_{25}OCOCH_2$-DTOA-Cu on a 5×10^{-3} M $CuSO_4$ solution is shown in Fig. 6.‡ By the measurements at lower temperature, 5 and 10 °C, two kinds of limiting areas, A_0^α and A_0^β in a larger (α) and a smaller (β) area region as shown in Fig. 6, were obtained. At a higher temperature A_0^α was not established clearly because of the disappearance of the α-region of the curves; the α-region might be attributed to the formation of the island structure. The A_0^β at each temperature were evaluated as follows: 52 Å² (25 °C), 56 Å² (16 °C), 60 Å² (10 °C), 64 Å² (5 °C). Contrary to the general relation between A and T, the A_0^β decreases with an increase in temperature. This unusual tendency can be explained by the slower dissolution of the unreacted ligand molecule at a lower temperature into the aqueous phase before the completion of the coordination reaction with cupric ions at a water surface. This implies that the dissolution of the ligand, even in such a slightly soluble one, should be responsible for the smaller apparent A_0 than the true value, and the same should be more probable for the more soluble other ligands. The true value of the limiting area for the ester ligand complex presumed experimentally by extrapolation might be about 65 Å² or more; this value is acceptable one if all the ligand molecules added on the water surface are assumed to exist there as the *cis* isomer and combine with cupric ions in a certain manner.

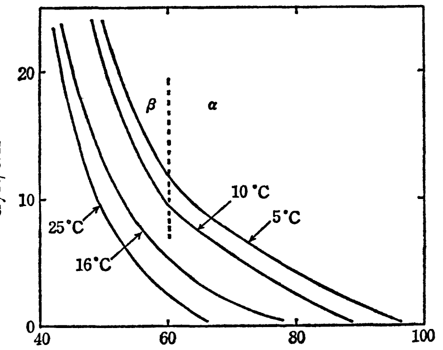

Fig. 6. The effect of temperature on π *vs.* A relation for $C_{12}H_{25}OCOCH_2$-DTOA-Cu on 5×10^{-3} M $CuSO_4$. Spreading solvent: benzene 2, hexane 3.

In the previous paper[4] we proposed the 'copper-acetate' type model which was a two-dimensional network for the compounds obtained by both the "bulk" and "monolayer" methods, namely the type A and B compounds. However this model is now obviously catastrophic as a model for the type B compounds by the following reasons: 1) by the calculation from the bond lengths it is concluded that this model requires only 30 Å² at most for a R–DTOA–Cu structure unit, but it is much smaller than above mentioned 65 Å², 2) 30 Å² for this model does not satisfy a condition to accomodate two hydrocarbon chains which is required in the B compounds, though the requirement is not needed in the A compounds. For the solution to the difficulty, a new model, named 'improved' model shown in Fig. 7, is proposed, and in this case a calculated area per R–DTOA–Cu unit is 60—70 Å² which agrees nicely with the observed limitting area for $C_{12}H_{25}OCOCH_2$–DTOA–Cu compound. For the type B compounds with other substituents R, we are not able to derive a suitable model from their small limitting areas experimentally obtained (22—25 Å²), however the 'improved' model

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‡ This operation was done mainly by Mr. Emoto.

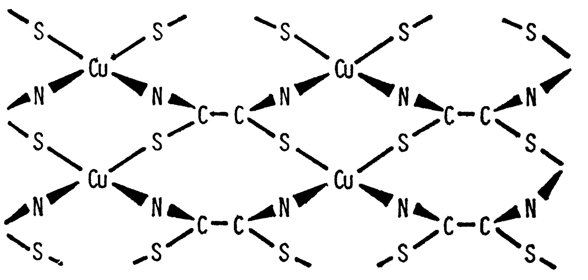

Fig. 7. "Improved model," the proposed molecular model of the stereospecific dithiooxamide copper coordination polymers.
Unevenness of its plane is indicated by a arrowhead affixed to a nitrogen atom.

can be also adopted to them with a certain confidence.

Built-up films. The complex monolayer was transferred from the water surface to the solid substrate by repeated dipping and withdrawing processes, the Langmuir and Blodgett method.[13] The coating of glass or quartz slides with Fe-stearate monolayers was effective for the tight fixation of the complex monolayers.

The uniform built-up films of Y type[13] of $C_{12}H_{25}$-$OCOCH_2$–DTOA–Cu complex were obtained but the other complexes, C_6H_{11}–, $C_6H_5CH_2$–, and $C_{12}H_{25}$–DTOA–Cu, were not uniformly transferred on to the solid substrates. With latters, defects in the surface of the multilayers were often appeared and could not be recovered.

The optical density of $C_{12}H_{25}OCOCH_2$–DTOA–Cu multilayers on quartz plates was measured in the visible and the ultraviolet region. The optical density was linearly increased with the number of films transferred. It means that transfer ratio from the water surface is the same for each monolayer. The absorption maximum was observed at 380 nm for $C_{12}H_{25}OCOCH_2$–DTOA–Cu compound.

The thickness of the built-up films estimated by observing the colors by reflected skylight is listed in Table 2. The relationship between the wavelength, λ, and the thickness of film, d, is given by an equation for an interface:

$$4d(n_2^2-n_1^2\sin^2\beta)^{1/2} = (2m-1)\lambda$$

where n_1 and n_2 are the refractive indexes of films and air, respectively, β is the incident angle measured and m is an integer.[14] The refractive index of the films was assumed to be $n_1=1.5$. The estimated value of thickness of a layer is reasonably explained by considering the molecular model of the compound.

Table 2. The thickness of a layer of $C_{12}H_{25}OCOCH_2$–DTOA–Cu estimated from the colors of reflection from the built-up films

Number of layers	Color	Thickness of a layer (Å)
40	yellow	22.3
50	reddish yellow	19.3
62	violet	20.5
72	green	21.7

The electric resistance of the built-up films was measured and will be published elsewhere.

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