

Self-Organization of a Dinuclear Metal Complex in Lyotropic Liquid Crystal: Ribbonlike Supramolecular Assemblies

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Received January 5, 1998. In Final Form: June 22, 1998

Self-organization behavior of a dinuclear metal complex, $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$, in water was investigated by cryo-transmission electron microscopy and atomic force microscopy (AFM). Very long ribbonlike supramolecular assemblies (300–1000 Å width and 1/10 thickness) were formed in lyotropic (nematic) liquid crystal and arrayed with a certain orientation. The two-dimensional small-angle neutron scattering showed an anisotropic pattern. The characteristic Bragg peaks were observed at $Q_{\text{peak}} = 0.018$ and 0.036 \AA^{-1} (interlayer distance = 350 Å). A Bragg peak in X-ray diffraction was observed at $2\theta_{\text{peak}} = 10.55^\circ$ (distance = 8.38 Å). The molecular order in the assemblies was confirmed by the nanometer observation of AFM. The molecular arrangement in the assemblies was discussed. Molecules interact through π - π stacking between phenanthroline rings, resulting in the formation of a sequential helical array along the assembly axis. In this arrangement, the long axis of the molecules orients along the assembly axis. In the direction normal to the assembly axis, tartrate cores arrange through hydrogen bonding.

Introduction

Organization of metal complexes has been attracting considerable interest in relation to the development of novel materials with unique physicochemical properties such as magnetization.^{1–4} The self-organization occurs even in water as well as in crystals.^{5–11} Polymeric and multidimensional structures of the complex-based assemblies were investigated by NMR,^{5–8,10} microscopy,⁶ spectroscopy,^{5,6,9} fast-atom-bombardment mass spectrometry,⁸ and X-ray crystallography.¹¹ Structural characterization of Langmuir–Blodgett films of a trinuclear cobalt cluster has already been carried out by using spectroscopy, atomic force microscopy (AFM), and X-ray scattering.¹²

In this work, supramolecular assemblies self-organized in aqueous solutions of a dinuclear metal complex, $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ (tart = tartrate(IV⁻), phen = 1,10-phenanthroline), were investigated by using microscopic and scattering/diffraction methods, and the molecular arrangement model in assemblies was proposed. Three of the present authors (N.K., M.I., and S.K.) and their collaborators^{6,7} reported that aqueous solutions of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ exhibit a liquid-crystalline phase at concentrations above 6 mM. Although properties of these anisotropic solutions were examined, molecular packing and arrangement in the aggregates were not revealed in the previous work.

Experimental Section

$\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ was synthesized by following the method of Robbins and Tapscott.¹³ Aqueous solutions of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ were prepared by dissolving powder in water at temperatures above 70 °C (Chart 1).

Microscopic observation was carried out on a BH optical microscope (Olympus Optical Co, Ltd.), a H-800 transmission electron microscope (TEM) (Hitachi, Ltd.), and a NanoScope III AFM (Digital Instruments). The procedures of TEM and AFM observation are described in detail elsewhere.^{14,15} Electron diffraction was observed at a camera length of 0.4 m on a H-800 electron microscope.

The small-angle neutron scattering (SANS) examination was performed on a WINK instrument of the National Laboratory of High Energy Physics and a SANS-U spectrometer installed at the Japan Atomic Energy Research Institute research reactor JRR-3M. The wide-angle X-ray diffraction was measured by a Rad-C diffraction instrument (Rigaku Elec. Ltd.).

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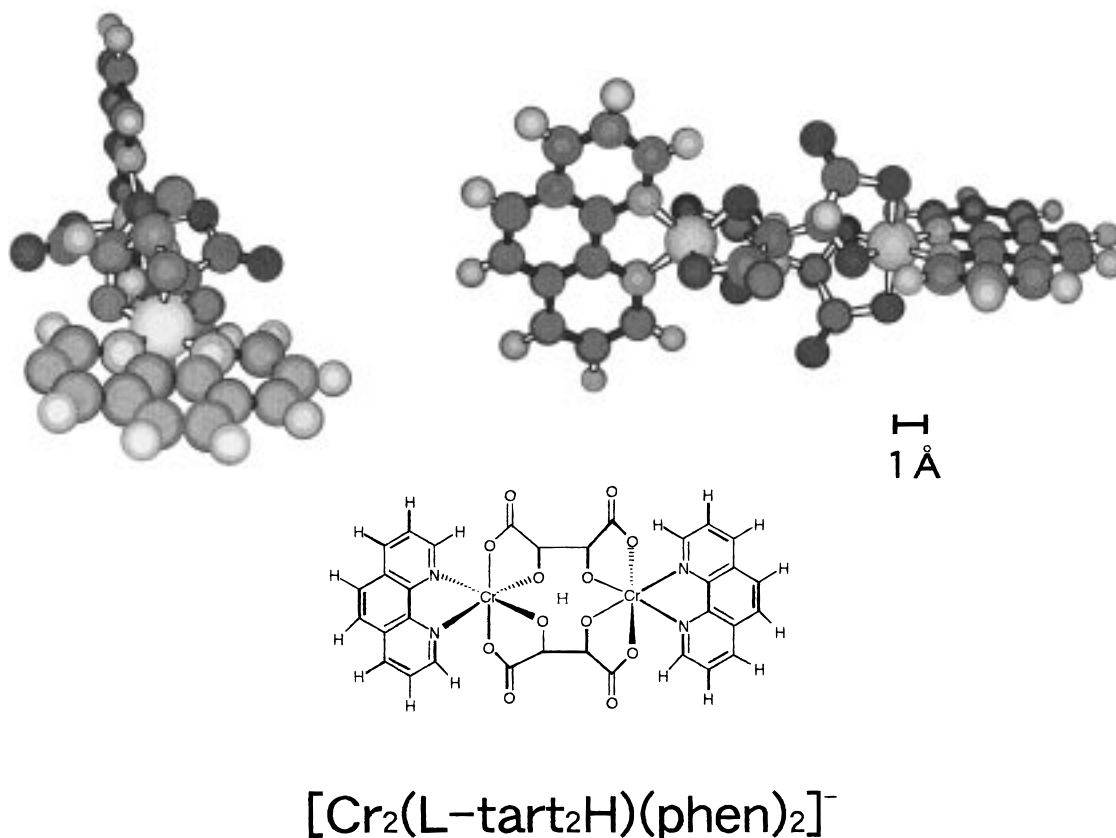
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Chart 1



Results

An optical microscopic observation under the crossed nicol was carried out for aqueous solutions of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$. For solutions at concentrations exceeding 6 mM, the formation of a nematic liquid crystal was elucidated from the polarized microscopic texture, as seen in Figure 1 (upper). A cryo-TEM photograph for a vitrified specimen prepared from an aqueous solution of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ at 6 mM is also given in Figure 1 (lower). Linear supramolecular assemblies of 300–800 Å width were observed. The assemblies were very long and arranged to a certain orientation. Similar texture of linear assemblies was confirmed even by the TEM observation for a freeze-fracture replica film of the solution. Electron diffraction of vitrified assemblies displayed three narrow rings and some reflection spots (see an insert in Figure 1), indicating the partly ordered molecular arrangement in the supramolecular assemblies.

Aqueous solutions of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ above 6 mM and its diluted ones at 0.6, 0.06, and 0.006 mM with water were dried at room temperature on freshly cleaved mica substrates and observed by AFM. The existence of linear assemblies was confirmed for all specimen, as illustrated in Figure 2. While the width of the assemblies was 400–1000 Å, the thickness was only 1/10 of the width. Therefore, the linearly associated assemblies must be ribbonlike in shape.

The ribbonlike assemblies in solutions above 6 mM were oriented to a certain direction, whereas the assemblies in diluted ones below 0.6 mM were disordered (see Figure 2). One can notice that the solutions, prepared by dissolving the sample powder directly into water at the same dilute concentrations, showed no ribbonlike aggregation behavior of the dinuclear complex, as previously reported.⁷

A similar AFM image of ribbonlike assemblies were also obtained from a specimen prepared by dissolving the sample powder in water at ca. 70 °C and successive drying on mica. The surface of the ribbonlike assembly was observed at a $200 \times 200 \text{ \AA}$ scale by AFM and is shown in Figure 3. The molecular organization on the surface could be conceived from the photograph, as estimated from the electron diffraction.

Figure 4 shows a two-dimensional (x - y plane) SANS profile for an aqueous (D_2O) solution of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ at 20 mM. The profile displayed the anisotropic diffraction pattern, in agreement with the formation of a nematic liquid-crystalline phase.¹⁶ The sectional SANS intensities $I(Q)$ at the x - and y -axes in Figure 4 are illustrated as a function of the scattering vector Q in Figure 5. The characteristic Bragg peaks were observed at $Q_{\text{peak}} = 0.018$ and 0.036 \AA^{-1} for both directions. The intensities were larger for the x -axis than for the y -axis. The same peaks were also detected for solutions at 40 and 12 mM. They correspond to the diffraction spacings at the ratio of $1:1/2$, suggesting the existence of layer structure. Then the interlayer distance of the (100) plane is 350 \AA ($=2\pi/0.018$). This value is equivalent to the spacing of the lateral organization of ribbonlike assemblies in the liquid-crystalline phase, as seen in Figure 1.

An aqueous solution of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ at 20 mM was dried on a glass substrate, and the wide-angle X-ray diffraction was measured as a function of the scattering angle 2θ . As seen in Figure 6, a strong Bragg peak at $2\theta_{\text{peak}} = 10.55^\circ$ (distance = 8.38 Å) was detected at a shorter distance than that at $2\theta_{\text{peak}} = 9.78^\circ$ (distance = 9.04 Å) for a powder sample. However, no significant

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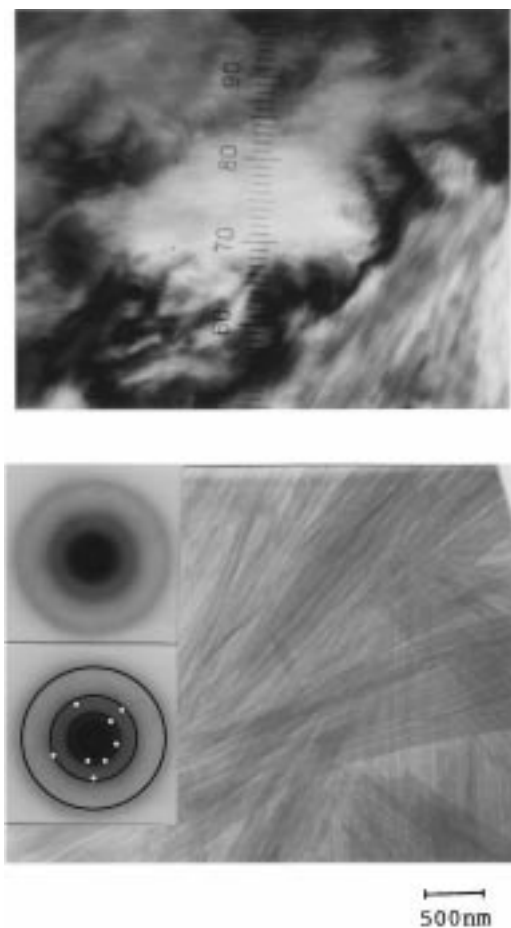


Figure 1. A polarized optical micrograph (upper) and a cryo-TEM photograph (lower) for an aqueous solution of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$. Upper: 20 mM concentration. Magnification is 40 \times . Lower: 6 mM concentration. An insert in TEM is an electron diffraction pattern (camera length 0.4 m) of same specimen and its schematic illustration.

Bragg peaks were observed at wider angles, which is in disagreement with the case of the powder.

Discussion

Ohba et al.^{1,2} and Sato et al.⁴ reported bimetallic assemblies which were formed through metal–CN–metal linkages. Lehn et al.^{5,8,9} and Bell and Jousselein¹⁰ found that double- and triple-helical assemblies were induced by the weaker and nondirectional interaction of an alkali-metal ion with organic ligands. Atencio et al.¹¹ proposed the columnar stacking structure which resulted from TI–TI and TI–O bonds between cores of disklike metal complexes. Dinuclear metal complexes in the present work must construct a novel-type of assemblies. The structure of molecular assemblies in the nematic liquid crystal of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ was recognized as ribbonlike by TEM and AFM. Moreover, the molecular arrangement on the assemblies was visualized as shown in Figure 3. There were the repeating distances of 21 Å along the assembly axis and of 8 Å in the almost perpendicular direction (ca. 100°). Three lower spots were arranged, by keeping about a 5 Å separation, between higher spots of the 21 Å repeating distance. The molecular length of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ is about 16.5 Å and the thickness is about 9 Å, while two phenanthroline residues tilt with a 100° scissor angle. On the basis of the molecular structure, its size, and the microscopic and diffractive results, the plausible molecular arrangement within

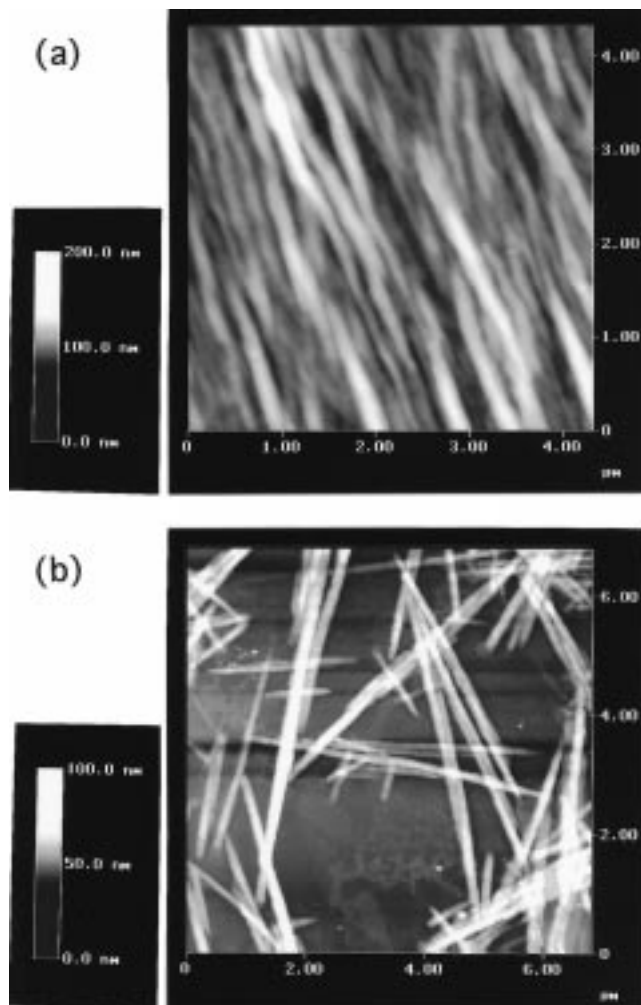


Figure 2. AFM images of specimen prepared from aqueous solutions of $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$. (a) 6 mM. (b) the diluted one (0.06 mM).

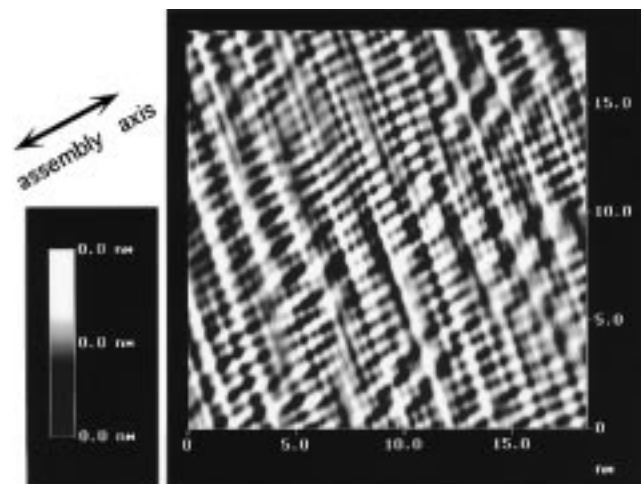


Figure 3. A high-resolution AFM image, at a 200 \times 200 Å scale, of a specimen which was prepared by dissolving $\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ in water at ca. 70 °C and successive drying on mica. The photograph was taken at the surface of a ribbonlike assembly.

assemblies in the liquid crystal was estimated as represented schematically in Figure 7.

$\text{Na}[\text{Cr}_2(\text{L-tart}_2\text{H})(\text{phen})_2]$ molecules interact with each other by π – π stacking between phenanthroline rings, resulting in the formation of a sequential helical array

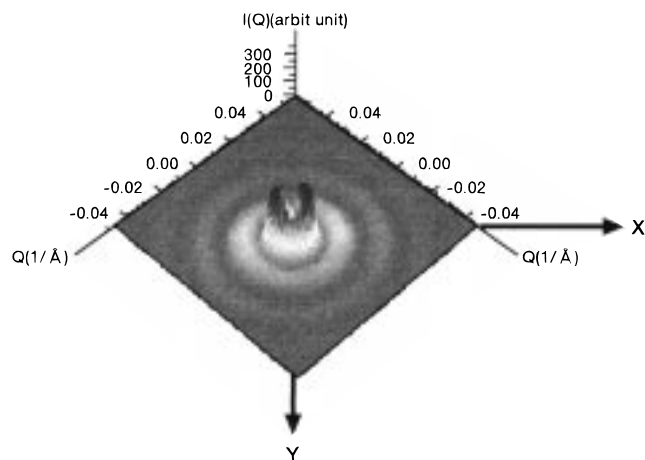


Figure 4. The two-dimensional SANS profile for an aqueous (D_2O) solution of $Na[Cr_2(L-tart_2H)(phen)_2]$ at 20 mM.

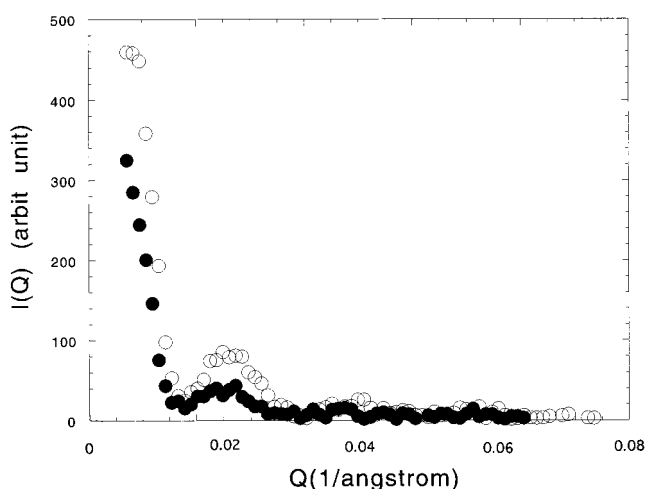


Figure 5. The sectional SANS intensities as a function of a scattering vector for an aqueous (D_2O) solution of $Na[Cr_2(L-tart_2H)(phen)_2]$ at 20 mM. \circ , x-axis; \bullet , y-axis (see Figure 4).

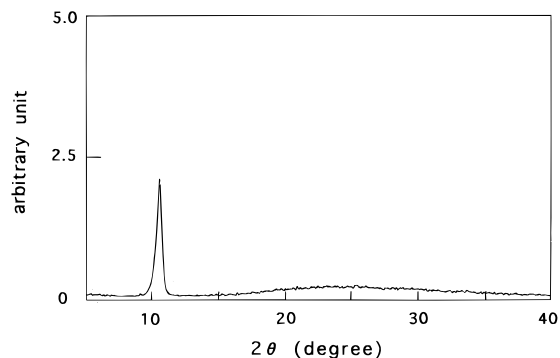


Figure 6. The wide-angle X-ray diffraction for a specimen prepared from an aqueous solution of $Na[Cr_2(L-tart_2H)(phen)_2]$ at 20 mM.

along the assembly axis. Then the long axis of the molecules orients along the assembly axis. The helical array must have a 10.5 Å helical pitch per molecule. Thus two higher spots at the 21 Å distance in the AFM image of Figure 3 correspond to the first and third stacked phenanthroline rings, and three lower spots with a 5 Å separation between them can be assigned to the second stacked phenanthroline rings and the adjacent tartrate cores.

In the direction normal to the assembly axis, hydrophilic tartrate cores of $Na[Cr_2(L-tart_2H)(phen)_2]$ are arranged

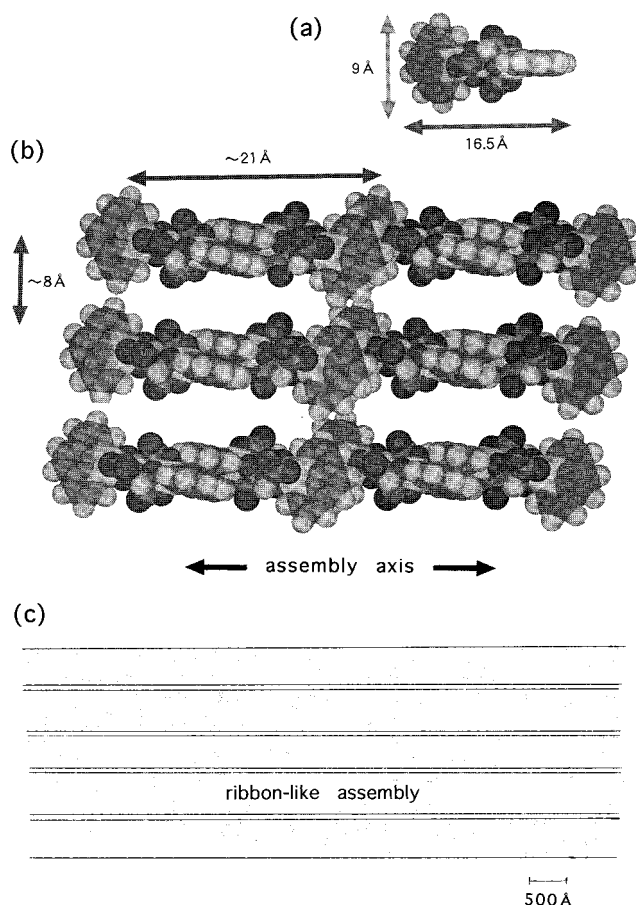


Figure 7. The schematic representation of (a) a molecule, (b) the molecular arrangement in a ribbonlike assembly, and (c) the assembly arrangement in a liquid-crystalline phase.

at a spacing of 8 Å. This distance was observed not only by AFM but also by X-ray diffraction. Since the overlapping distance of π electrons is 3.4 Å, the repeating distance of 8 Å is too long for the sequential π - π stacking interaction to occur. Therefore, in the direction normal to the assembly axis, tartrate cores interact by hydrogen bonding directly or through hydrated water. The 10° tilt angle of the array from the normal direction is owing to the geometrical slip of hydrogen-bonded tartrate cores in the adjacent helical arrays. The hydrogen bonds between the tartrate cores are partly cut by the insertion of water molecules. Then the molecular organization at the direction normal to the assembly axis may be loosened in aqueous solutions.

The polymeric, helical arrays consisting of intermolecular π - π stacking make a three-dimensional network by hydrogen bonding between cores of metal complexes to form ribbonlike assemblies. The assemblies have the finite width and thickness, although the length is very long. The array of ribbonlike assemblies at a certain direction is kept by the lateral interaction between them. The repeating separation in the lateral direction was determined as 350 Å by SANS. The spatial ordering of ribbonlike assemblies results in the anisotropy of solutions, that is, a lyotropic (nematic) liquid crystal.

If sodium ions are incorporated in the ribbonlike assemblies, the dinuclear metal complex ions can interact electrostatically with sodium ions. Such an interaction, however, can be easily ruled out, since counterionic sodium ions are not localized in assemblies but dissociate partly in solutions. As the experimental fact, the distance between helical arrays in assemblies was shorter than

that in powder, as described above. The structural distortion from crystals to liquid crystals has already been reported in the self-organization of thallium(I) β -diketonates.¹¹

Acknowledgment. The authors are grateful to Prof. K. Komoto and Mr. T. Iwamoto of Nagoya University for their generous permission to use the wide-angle X-ray

diffraction instrument and the electron microscope, respectively. We also wish to thank Prof. M. Furusaka of the National Laboratory of High Energy Physics and Prof. E. Matsushita and Dr. M. Imai of Tokyo University for their permission and help in measuring SANS.

LA9800194