Langmuir **2001,** *17,* 361−368

Effect of Counterions on the Ribbonlike Supramolecular Assembly Formation of Dinuclear Metal Complexes in the Lyotropic Mesophase

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Received March 31, 2000. In Final Form: July 7, 2000

The effect of counterions on the formation of the ribbonlike supramolecular assembly of a dinuclear metal complex in the lyotropic mesophase has been examined by optical microscopy, cryo-transmission electron microscopy, atomic force microscopy, and X-ray diffraction. Potassium and ammonium salts of $[Cr_2(\text{L-tart}_2H)(phen)_2]^-$ (tart = tartrate(IV−), phen = 1,10-phenanthroline) in water display liquid crystals, where ribbonlike assemblies are formed like that of the sodium salt. Sheetlike assemblies are found in dilute solutions of sodium, potassium, and ammonium salts. On the other hand, aqueous solutions of $[Co(en)_3]^{3+}$ (en = ethylenediamine) salts do not display liquid crystals because of the nonrigid character of the ribbons. The $[Co(en)_3]^{3+}$ salts form sheets and ribbonlike assemblies in the same solution. The ribbons gather like strings or roll spirally. The characteristic assembly formation of $[Co(en)_3]^{3+}$ salts may originate in the bulky structure of $[Co(en)_3]^{3+}$.

Introduction

Typical lyotropic liquid crystals are classified into hexagonal (middle) and lamellar (neat) phases, which are formed in the solutions of surfactants.[1,2] However, the classes are not limited to the typical cases, and the lyotropic liquid crystals in some cases are in the nematic or cholesteric arrangements; α-helical poly-γ-benzyl-L-glutamate forms cholesteric liquid crystals in organic solvents,[2] and the liquid crystal of oligo-γ-benzyl-L-glutamate in the β-conformation in organic solvents is nematic.[3] Azo-dye surfactant[4] and water-soluble azo-dye[5] display nematic liquid crystals in aqueous methanol solutions.

Recently, we reported novel liquid crystal formation by metal complexes.[6−8] The dinuclear metal complex $Na[Cr_2(\text{L-tart}_2H)(phen)_2]$ (tart = tartrate(IV−), phen = 1,10-phenanthroline) in water forms very long ribbonlike supramolecular assemblies in the lyotropic liquid crystal.[8] Assemblies are arrayed with a certain orientation in the nematic liquid crystal. Molecules in the assemblies interact through $\pi-\pi$ stacking between phenanthroline rings, resulting in the formation of a sequential helical array along the assembly axis, along which the long axis of the molecule orients. In the direction normal to the assembly axis, tartrate cores are arranged through hydrogen-bonding. In this arrangement, the situation and location of sodium ions are uncertain, because a strong Bragg peak around $2\theta_{\text{peak}} = 10°$ is detected at a larger angle (that is, at a shorter distance) in the assembly than in powder.[8]

In the present paper, we investigate the effect of counterions on the formation of the ribbonlike assembly of a dinuclear metal complex in the lyotropic mesophase. Potassium, ammonium, and $[Co(en)_3]^{3+}$ (en = ethylenediamine) salts of the dinuclear metal complex ion $[Cr_2(\text{L-tart}_2H)(phen)_2]^-$ are examined in water by optical microscopy, cryo-transmission electron microscopy (TEM), atomic force microscopy (AFM), and X-ray diffraction. The structures of molecular assemblies formed by molecules with different counterions are determined and compared with each other and with that of the sodium salt.

Experimental Section

The synthesis of $[Cr_2(\text{L-tart}_2H)(phen)_2]^-$ salts followed the method of Robbins and Tapscott.[9] The counterions are Na^+, K^+, NH_4^+, and three kinds of $[Co(en)_3]^{3+}$, that is, Λ-$(+)_D$-$[Co(en)_3]^{3+}$, Δ-$(-)_D$-$[Co(en)_3]^{3+}$, and $\Delta\Lambda$-$(\pm)_D$-$[Co(en)_3]^{3+}$, the metal complexes of which are denoted as the (+), (−), and (±) species, respectively. Aqueous solutions of $[Cr_2(\text{L-tart}_2H)(phen)_2]^-$ salts were prepared

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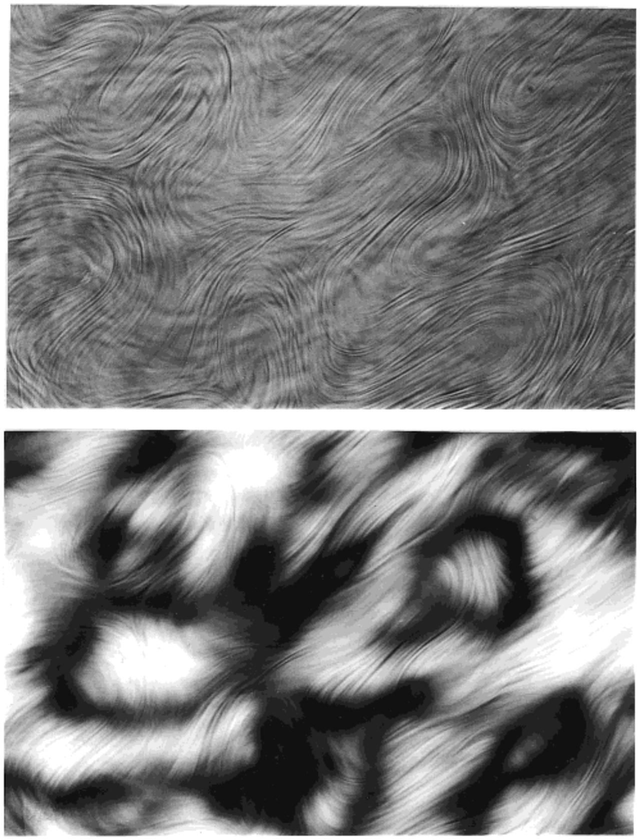

Figure 1. Optical microscopic photographs of an aqueous 40 mM solution of Na[Cr_2(L-tart$_2$H)(phen)$_2$]: (top) without crossed polarizers and (bottom) under crossed polarizers. The magnification is 100×.

by dissolving powder in water at a temperature above 70 °C and cooling to room temperature (~25 °C). Aqueous solutions of [Co(en)$_3$][Cr_2(L-tart$_2$H)(phen)$_2$]$_3$ were maintained for more than 1 day at room temperature after they were cooled, until fibrous assemblies were visualized. The concentration of the aqueous solutions denotes the molarity of the salts.

Microscopic observation was carried out on a Nikon Optiphot-2 optical microscope equipped with a differential interference contrast optic (Nomarski prism) and crossed polarizers, a Nikon Y2BP optical microscope equipped with crossed polarizers, a Hitachi H-800 TEM, and a Digital Instruments NanoScope III AFM. Detailed procedures of cryo-TEM and AFM observations are described in the literature.[10,11] Wide-angle X-ray diffraction was measured with a Rigaku Rad-C diffraction instrument. Drops of solution on a glass slide were supplied for the optical microscopic observation at room temperature. A solution for the cryo-TEM was vitrified in slushed nitrogen and observed at nitrogen temperature. After solutions were kept at room temperature for a minute on freshly cleaved mica and glass substrates, those were drained. Then, the specimens on the substrates were dried at room tempearature for 8 h in vacuo before they were used for AFM observation and X-ray diffraction measurement.

Results

Sodium, Potassium, and Ammonium Salts. Optical microscopic observation was performed for aqueous solutions of Na[Cr_2(L-tart$_2$H)(phen)$_2$], and the photographs with and without crossed polarizers for a solution at 40 mM concentration are shown in Figure 1. The colored liquid crystal texture under polarization and the lined pattern under nonpolarization were observed. A similar texture has been reported for solutions at concentrations down to 6 mM and was elucidated to be due to nematic liquid crystals.[6,8] The same kinds of liquid crystal mesophases were observed even for potassium and ammonium salts in the present work.

AFM images were observed for specimens prepared from aqueous 6 mM solutions of sodium, potassium, and ammonium salts of [Cr_2(L-tart$_2$H)(phen)$_2$]$^-$. Linear assemblies were visible in the AFM images for all solutions of three kinds of salts, as seen in Figure 2. The surface of a linear assembly of the potassium salt was observed, and the molecular organization on the assembly was elucidated from an AFM image at a 20×20 nm^2 scale, which is given in Figure 3.

AFM images were also taken for specimens prepared from aqueous 0.2 mM solutions of salts of [Cr_2(L-tart$_2$H)(phen)$_2$]$^-$, and an image for the sodium salt is exemplified in Figure 4. No linear assemblies were observed, but sheetlike flat terraces existed commonly for all specimens from the three salts. Although the sizes of the sheets varied, their height was common at 0.7−1.1 nm, which was evaluated from the section analysis. The small sheets with similar height were also found on the wide sheet.

The wide-angle X-ray diffraction was measured as a function of the scattering angle 2θ for specimens prepared from liquid crystal mesophases (6 mM) of sodium and ammonium salts as well as powder diffraction. A strong Bragg peak was detected at $2\theta_{\text{peak}} = \sim 10°$ for all systems. However, no significant Bragg peaks were observed at wider angles for liquid crystals, different from powder diffraction. Numerical values of $2\theta_{\text{peak}}$ and distance d are listed in Table 1. The distance in the liquid crystal was shorter than that in powder, and the distance for the ammonium salt was slightly shorter than that for the sodium salt.

[Co(en)$_3$]$^{3+}$ Salts. Aqueous 0.3 and 3 mM solutions of [Co(en)$_3$][Cr_2(L-tart$_2$H)(phen)$_2$]$_3$ were maintained at room temperature after being prepared at high temperature. Hot solutions became turbid after they were cooled to room temperature. Before long, fibrous assemblies were formed in the solutions, and they were sedimentated into the bottom of the vessel after overnight. The fibrous assemblies, which were visually recognizable and stable, at least for a few days, were less in amount for a 0.3 mM solution than for a 3 mM solution. The fibrous assemblies and their bundles were observed on an optical microscope, as shown in Figure 5, but there was no texture of an anisotropic mesophase.

Figure 6 shows cryo-TEM photographs of aqueous solutions of [Co(en)$_3$][Cr_2(L-tart$_2$H)(phen)$_2$]$_3$. There was no difference between the textures in the 0.3 and 3 mM solutions. Fibers and flat sheets were observed in a solution of the (+) species. The fibers seemed to be tapelike ribbons and were found even in solutions of the (−) species. The ribbons were gathered like strings or rolled into spirals, although the spirals were minor. The tapelike ribbons of the (±) species were rather thick, and no spiral ribbons were found, different from the (+) and (−) species. Ribbons observed by cryo-TEM were 0.05−3 μm in width, the size of which was consistent with the observation by optical microscope. The distance calculated from wide-angle X-ray diffraction of a specimen prepared from an aqueous 3 mM solution of fibers of the (+) species was 0.950 nm, longer than those of the sodium and ammonium salts, as compared in Table 1.

Figure 7 shows AFM images for specimens prepared from aqueous 0.3 and 3 mM solutions of Δ-(−)$_D$-[Co(en)$_3$][Cr_2(L-tart$_2$H)(phen)$_2$]. Tapelike ribbons and flat sheets were observed in both solutions. Those assemblies were

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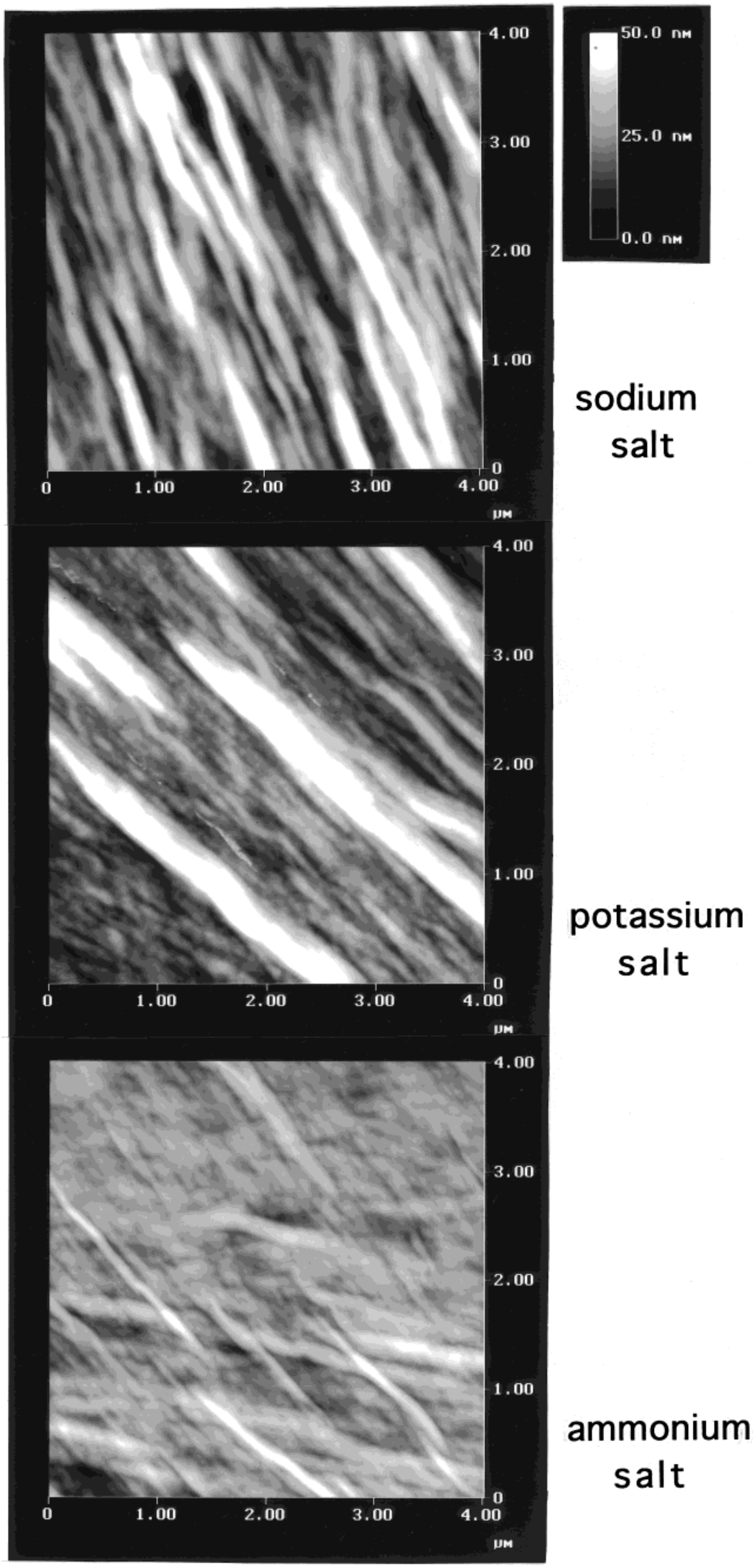

Figure 2. AFM images of specimens prepared from aqueous 6 mM solutions of the sodium, potassium, and ammonium salts of $[Cr_2(\text{L-tart}_2H)(phen)_2]^-$.

already confirmed by cryo-TEM. The width of the tapelike ribbons was less than 2 μm, which was comparable to that obtained by cryo-TEM. The thickness of the flat sheets was only 0.8−2.2 nm.

Discussion

In the previous paper, we reported that aqueous solutions of $Na[Cr_2(\text{L-tart}_2H)(phen)_2]$ display a liquid

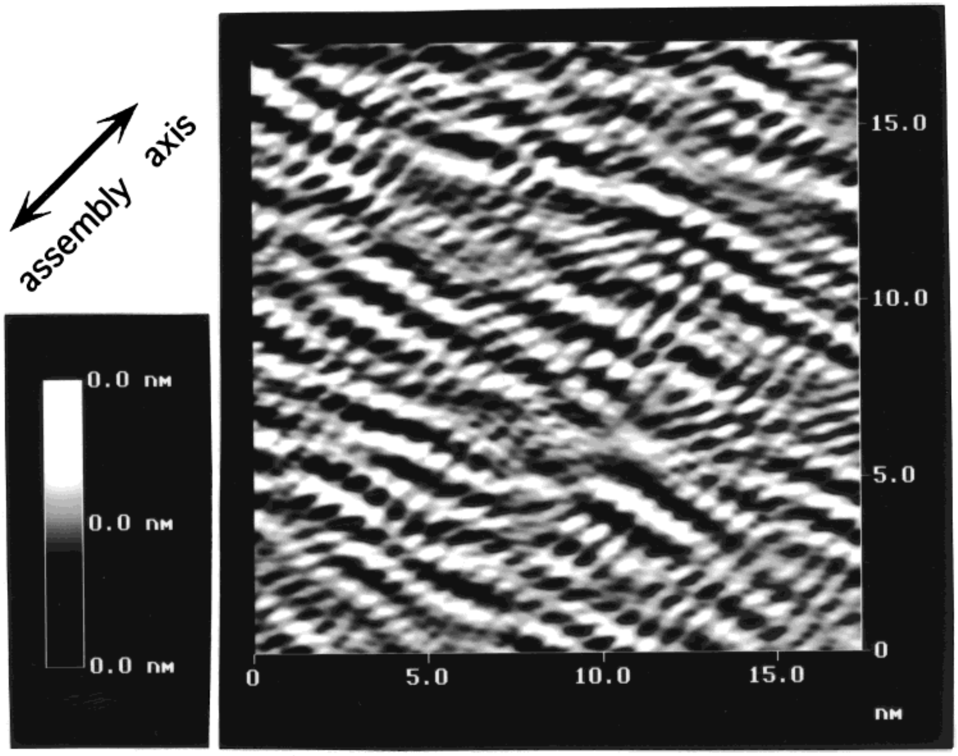

Figure 3. An AFM image of a specimen prepared from an aqueous 6 mM solution of K[Cr_2(L-$tart_2$H)$(phen)_2$]. The image was taken at the surface of a ribbonlike assembly.

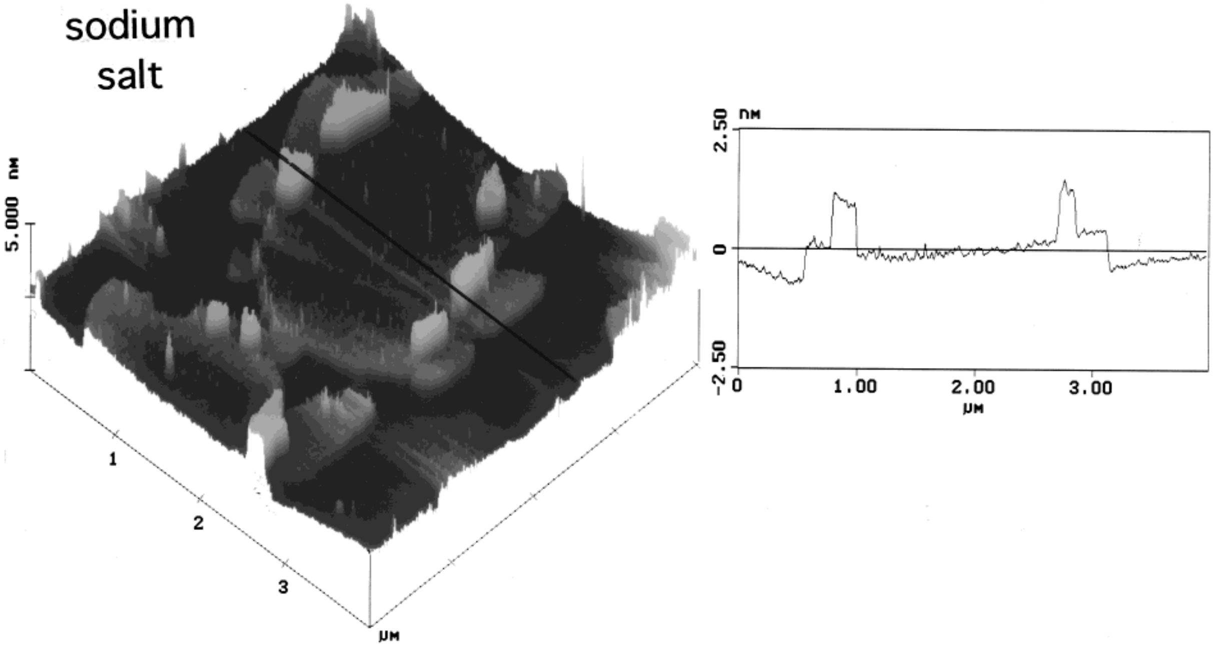

Figure 4. An AFM image and a section analysis of a specimen prepared from an aqueous 0.2 mM solution of Na[Cr_2(L-$tart_2$H)-$(phen)_2$].

Table 1. $2\theta_{peak}$ and Distance d in Wide-Angle X-ray Diffraction

condition	sample	$2\theta_{peak}$, deg	d, nm
powder	Na^+ salt	9.83	0.899
	NH_4^+ salt	10.04	0.880
liquid crystal (6 mM soln)	Na^+ salt	10.64	0.831
	NH_4^+ salt	10.76	0.822
fiber (3 mM soln)	(+)-$[Co(en)_3]^{3+}$ salt	9.30	0.950

crystal mesophase at concentrations above 6 mM.[8] The fibrous structure of Na[Cr_2(L-$tart_2$H)$(phen)_2$] in the liquid crystal has been confirmed from cryo-TEM, AFM, and so forth. The assemblies have a 30−100 nm width and a thickness of only 1/10 scale. Therefore, they must be ribbonlike in shape. They are very long and aligned to a certain direction, following the formation of nematic liquid crystals in the concentrated solutions. The structure of assemblies in the liquid crystal may be similar, at least up to a 40 mM concentration.

It was confirmed in the present work that the ribbonlike assemblies of potassium and ammonium salts are similar to those of the sodium salt. K[Cr_2(L-$tart_2$H)$(phen)_2$]

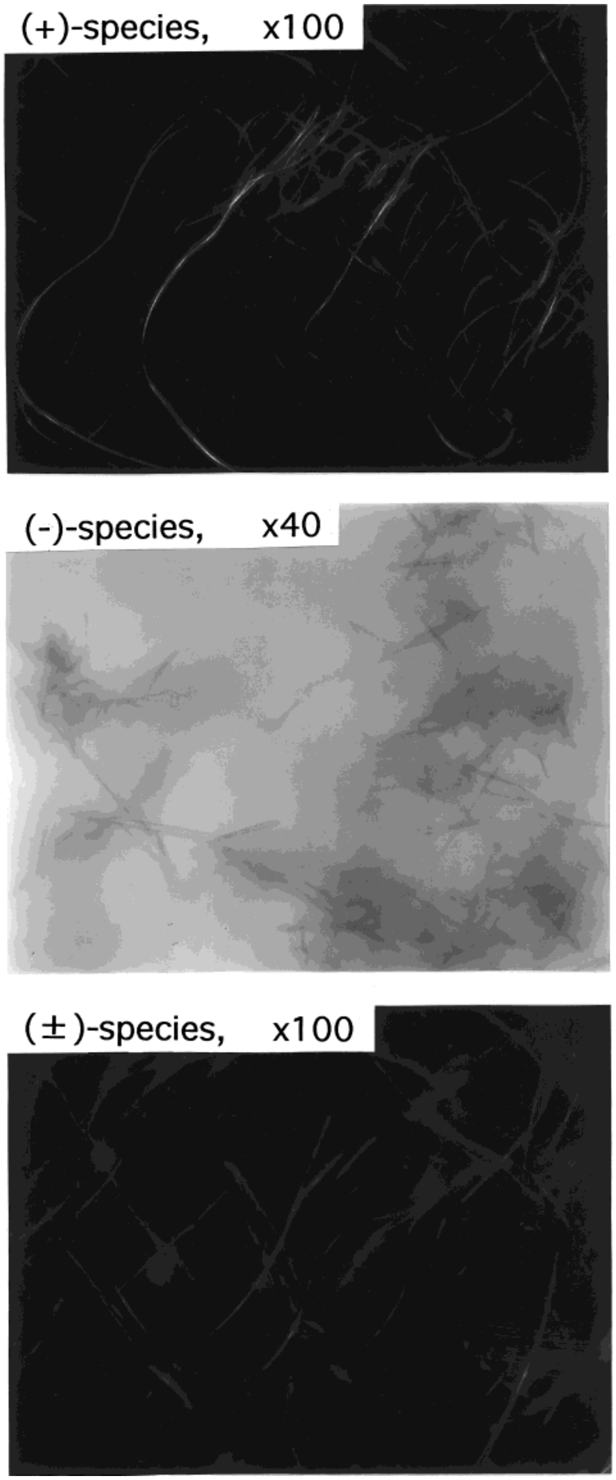

Figure 5. Optical microscopic photographs of aqueous 3 mM solutions of $[Co(en)_3][Cr_2(\text{L-tart}_2H)(phen)_2]_3$. The numerical values indicate the magnification. The photographs were taken by an optical microscope with crossed polarizers for the (+) and (±) species and with a Nomarski prism for the (−) species.

molecules are fairly organized on the surface of the ribbonlike assembly, as clarified by AFM. A more organized arrangement is obtained on the surface of a ribbonlike assembly prepared by dissolving powder in water at a high temperature and successively drying on substrate.[8] It is apparent from the comparison of AFM images at nanoscale that the molecular arrangement in assemblies of the potassium salt is like that of the sodium salt. Therefore, the molecular arrangement illustrated in Figure 7 of ref 8 must be common for assemblies of sodium, potassium, and ammonium salts.

Molecular assemblies in solution freshly prepared at a dilute concentration in the present work are different from those in the dilution of the liquid crystal mesophase, which was previously reported.[8] Different from linear ribbonlike assemblies in the dilution, sheetlike assemblies of flat and wide domains appear in the AFM images from freshly prepared solutions of sodium, potassium, and ammonium salts. Because the height (0.7−1.1 nm) of the sheet is close to the width (0.9 nm)[8] of $[Cr_2(\text{L-tart}_2H)(phen)_2]^-$ and is lower than the length (1.65 nm),[8] ions in the sheet must lie on the substrate. An ordered arrangement of lying molecules, which was previously drawn,[8] is presented as a model of the molecular arrangement on the ribbonlike assemblies. Then, the sheets may be a predecessor of ribbonlike assemblies.

Two types of assemblies were found for $[Co(en)_3][Cr_2(\text{L-tart}_2H)(phen)_2]_3$. One is sheetlike assemblies with 0.8−2.2 nm thickness and with different sizes and shapes, which are similar to the sheets of the sodium, potassium, and ammonium salts of $[Cr_2(\text{L-tart}_2H)(phen)_2]^-$ in the dilute solutions. The sheetlike assemblies must be only monolayers or bilayers of $[Co(en)_3][Cr_2(\text{L-tart}_2H)(phen)_2]_3$. Another is ribbonlike assemblies with a width less than a few micrometers. The ribbons always coexist with the sheets in solutions, different from the relation between ribbons and sheets of the sodium, potassium, and ammonium salts of $[Cr_2(\text{L-tart}_2H)(phen)_2]^-$. Because the ribbons of $[Co(en)_3][Cr_2(\text{L-tart}_2H)(phen)_2]_3$ should be very thin like sheets, they easily gather to strings or roll to spirals, but strings or spirals were not found for fibers of the sodium, potassium, and ammonium salts of $[Cr_2(\text{L-tart}_2H)(phen)_2]^-$ because of their thicker character.

The spiral assemblies are formed by the (+) and (−) species but not by the (±) species. A similar relation has been reported for assemblies of chiral amphiphilic molecules. Fibrous assemblies of 12-hydroxystearic acid, *n*-alkyl-glucone amido, and *N*,*N*′-bis[1-carbonyl-12-hydroxyoctadecyl]butane diamine have right-handed helical sense for D-species and left-handed helical sense for L-species.[12−14] Reverse senses were reported for *N*-(2-hydroxydodecyl)amino acid, cationic double-tailed amino acid amphiphiles, and *N*-octylgalactone amido.[14−17] The DL species of all amphiphiles form nonhelical assemblies. One of authors (T. I.) and her collaborators found that *N*-acyl-L-aspartic acids form fibrous assemblies with right-handed helical sense.[10,18,19] Gulik-Krzywicki et al.[20] investigated supramolecular polymers formed from complementary chiral components. The results showed that the molecular chirality is translated into the supramolecular helicity.

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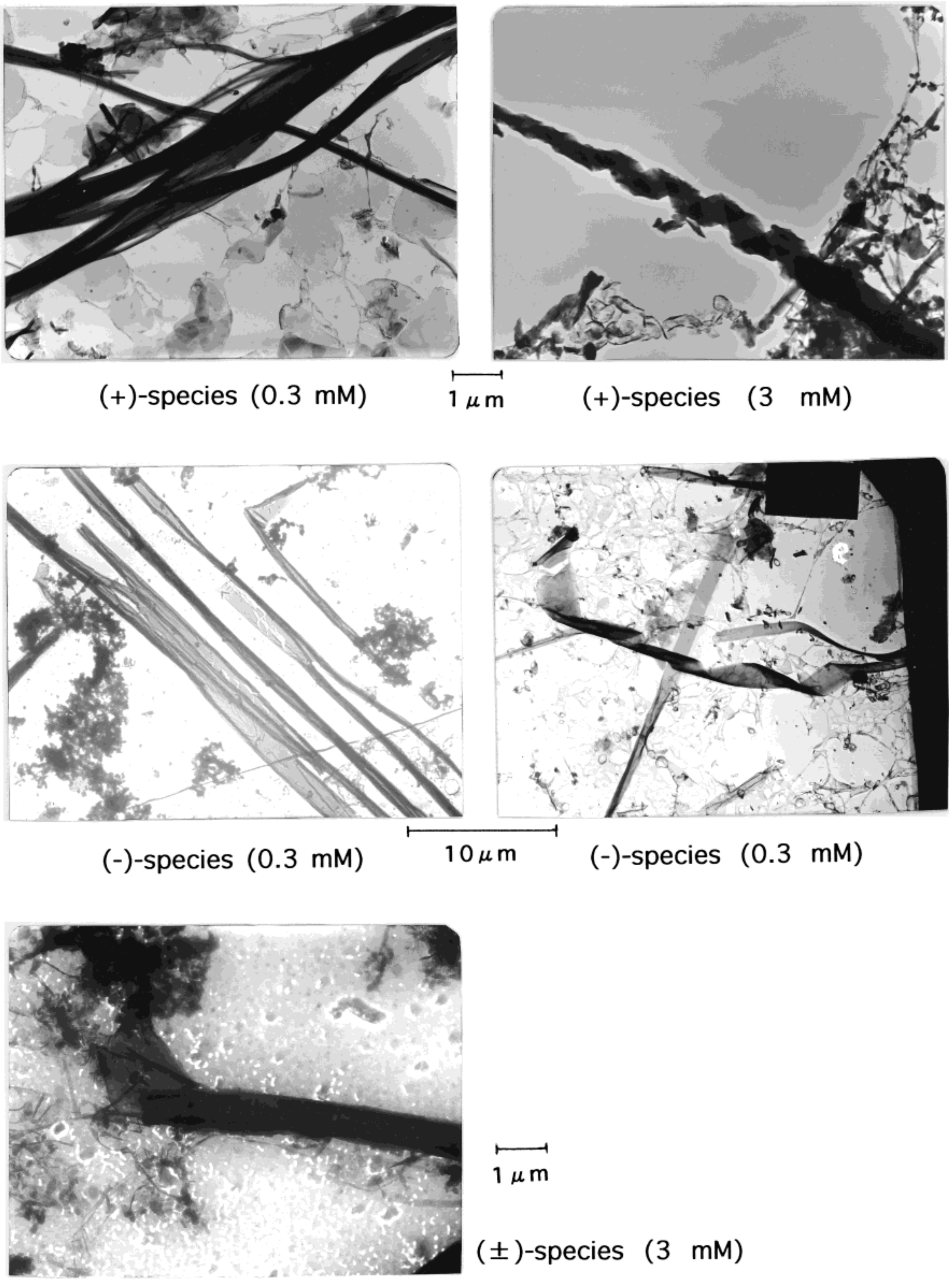

(+)-species (0.3 mM) (+)-species (3 mM)

(-)-species (0.3 mM) (-)-species (0.3 mM)

(±)-species (3 mM)

Figure 6. Cryo-TEM photographs of aqueous 0.3 and 3 mM solutions of $[Co(en)_3][Cr_2(\text{L-tart}_2H)(phen)_2]_3$.

It should be noticed that the sodium, potassium, and ammonium salts of $[Cr_2(\text{L-tart}_2H)(phen)_2]^-$ form liquid crystals, whereas $[Co(en)_3][Cr_2(\text{L-tart}_2H)(phen)_2]_3$ does not. A rigid structure of molecular assemblies is necessary to form nematic liquid crystals. Because fibrous assemblies of $[Co(en)_3][Cr_2(\text{L-tart}_2H)(phen)_2]_3$ are not rigid, as seen in optical and electron microscopic photographs, they prefer entanglement rather than the liquid crystal formation. The distance observed from wide-angle X-ray diffraction for powders of the sodium and ammonium salts is longer than that for liquid crystals of the sodium and ammonium salts but shorter than that for fiber solutions of the $[Co(en)_3]^{3+}$ salts. It may be referred that the counterions such as sodium and ammonium ions are dissociated from the molecular assemblies in the liquid crystal, whereas they are included in their crystals. On the other hand, $[Co(en)_3]^{3+}$ must be incorporated in the assemblies in solution, different from the sodium and ammonium salts. However, the location and participation of the respective ions cannot be clarified in the present work.

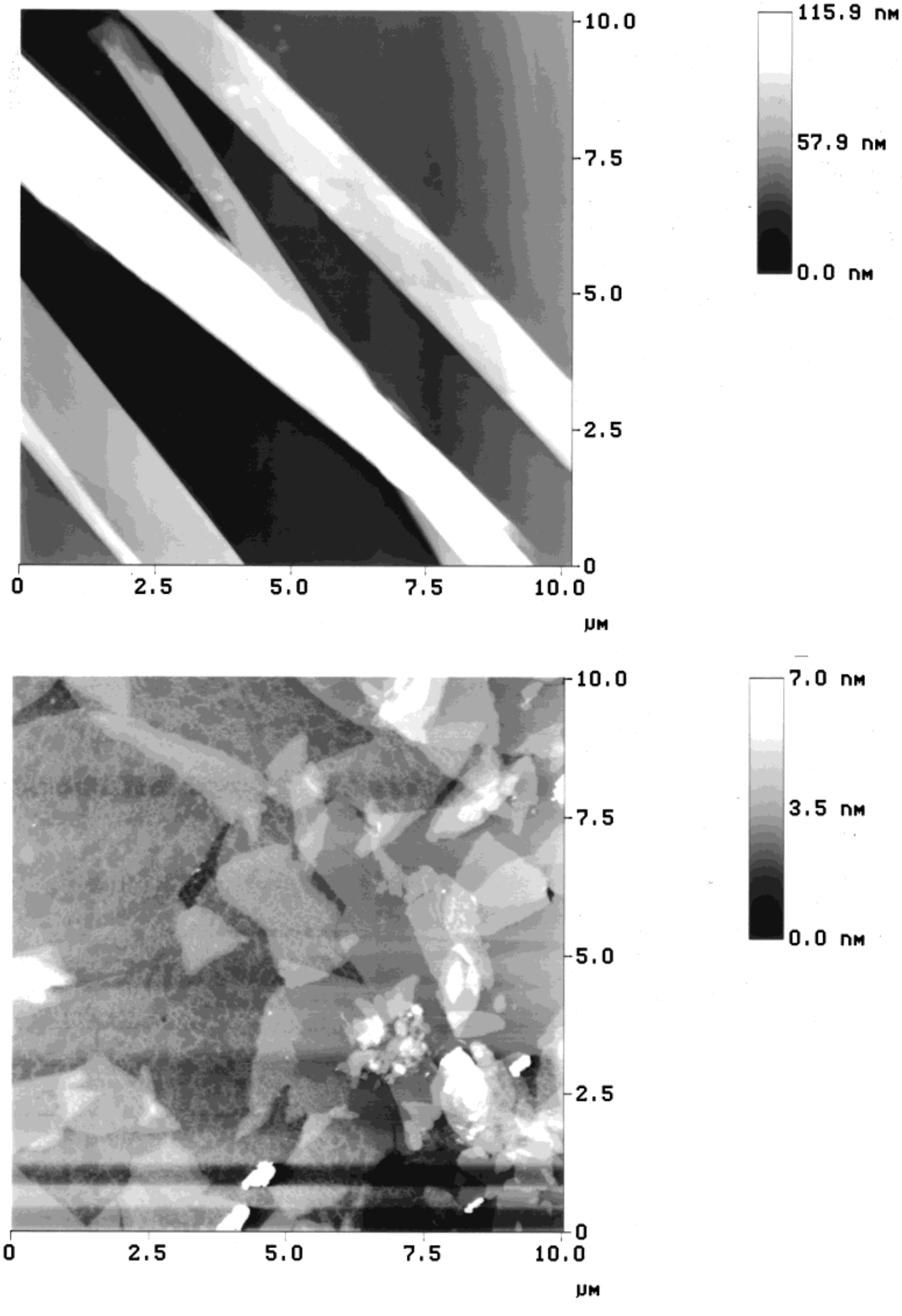

Figure 7. AFM images of specimens prepared from aqueous solutions of Δ-(−)$_D$-[Co(en)$_3$][Cr$_2$(L-tart$_2$H)(phen)$_2$]$_3$: (top) 0.3 mM and (bottom) 3 mM.

Conclusions

It was confirmed from microscopic observations for aqueous solutions of dinuclear metal complexes, potassium and ammonium salts of [Cr$_2$(L-tart$_2$H)(phen)$_2$]$^-$, that a nematic liquid crystal mesophase was formed at high concentration as well as for a sodium salt. The molecular arrangement of ribbonlike assemblies in the mesophase was also like that of the sodium salt. Sodium, potassium, and ammonium salts of [Cr$_2$(L-tart$_2$H)(phen)$_2$]$^-$ also formed sheetlike assemblies with monolayer thickness in the dilute solution.

On the other hand, in aqueous solutions of [Co(en)$_3$][Cr$_2$(L-tart$_2$H)(phen)$_2$]$_3$ ribbonlike assemblies coexist with sheetlike assemblies. The sheets are constructed by monolayers or bilayers and are similar to the sheets of the sodium, potassium, and ammonium salts of [Cr$_2$(L-tart$_2$H)(phen)$_2$]$^-$. The ribbonlike assemblies of [Co(en)$_3$][Cr$_2$(L-tart$_2$H)(phen)$_2$]$_3$ are rather thinner than the ribbons of the sodium, potassium, and ammonium salts and therefore gather or roll. Such thin ribbons cannot form liquid crystals.

In the molecular assemblies investigated so far, the formation of lyotropic liquid crystals by molecular assemblies of metal complexes is novel.[21] The liquid crystal formation depends on counterions. Ribbonlike assemblies of $[Co(en)_3][Cr_2(\text{L-tart}_2H)(phen)_2]_3$ present helical sense. The formation of helical fibers from amphiphiles lacking alkyl chains is unique.

Acknowledgment. The authors are grateful to Professor K. Komoto and Mr. T. Iwamoto of Nagoya University for their generous permission to use a wide-angle X-ray diffraction instrument and an electron microscope, respectively.

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