Formation of Thermotropic and Lyotropic Liquid Crystals of Bis(*N*-alkylethylenediamine)silver(I) Nitrate

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We have synthesized bis(*N*-hexylethylenediamine)silver(I) nitrate ([Ag(hex-en)$_2$]NO$_3$), bis(*N*-octylethylenediamine)silver(I) nitrate ([Ag(oct-en)$_2$]NO$_3$), and bis(*N*-dodecylethylenediamine)silver(I) nitrate ([Ag(dod-en)$_2$]NO$_3$) and investigated the aggregation behavior of [Ag(dod-en)$_2$]NO$_3$ and [Ag(oct-en)$_2$]NO$_3$ in the liquid state. An X-ray crystallographic analysis revealed that [Ag(dod-en)$_2$]NO$_3$ has a dinuclear structure in the crystalline state — the molecular composition unit is [Ag$_2$(dod-en)$_4$](NO$_3$)$_2$, where the two dod-en ligands bridge two silver ions that are coordinated by four nitrogen atoms. The dinuclear complex is appreciably dissociated into a mononuclear complex in solution. It was found that [Ag(oct-en)$_2$]NO$_3$ and [Ag(dod-en)$_2$]NO$_3$ form thermotropic liquid crystals in the temperature ranges 48–67 °C and 59–96 °C, respectively, and a lyotropic liquid crystal was also observed for [Ag(dod-en)$_2$]NO$_3$ in *n*-heptane at around room temperature in the presence of a small amount of water. The structures of the thermotropic and lyotropic liquid crystals of [Ag(dod-en)$_2$]NO$_3$ were identified as a typical smectic A (S$_A$) type and a nematic one, respectively.

Introduction

The field of metallomesogens has developed rapidly in recent years.[1−5] Despite this, however, the lyotropic behavior of thermotropic metallomesogens has rarely been studied.[3−5] Furthermore, although metallosurfactants have characteristic structures and unique properties that are not seen in conventional surfactants, detailed and systematic studies on their aggregation behavior in solutions have not been carried out even for simple types of surfactants.[6−11]

Bis(*N*-alkylethylenediamine)metal complex surfactants form a variety of aggregates, since they have a delicate hydrophile-lipophile balance, and their double-chained molecular shape is favorable for the formation of highly ordered aggregates.[8−11] They easily form aggregates with appropriate amounts of encapsulating water in organic solvents of low dielectric constant, such as benzene and chloroform. One (M. Iida) of the present authors and coworkers has systematically investigated the physical properties and structural characterizations of highly aggregated systems such as bis(*N*-alkylethylenediamine)zinc(II), with various anions, dichlorobis(*N*-octylethylenediamine)cadmium(II), and bis(*N*-octylethylenediamine)palladium(II) chloride complexes in water/benzene or water/chloroform systems.[10,11] In a series of these studies, we have revealed the change in the geometry of the hydrocarbon chains of *N*-octylethylenediamine ligands in the zinc(II) complex from *transoid* to *cisoid* upon transfer from the crystalline state to the water/benzene interface in a microemulsion using Atomic Face Microscope (AFM) and Transmission Electron Microscope (TEM) methodologies.[10,11b,11c] Furthermore, the same group has synthesized and isolated bis(*N*-hexadecylethylenediamine)silver(I) nitrate ([Ag(hexd-en)$_2$]NO$_3$).[12] This complex is highly soluble in neat *n*-heptane and can be reduced in contact with an aqueous sodium borohydride solution to form silver(0) nanoparticles. An assembly of the silver ions of [Ag(hexd-en)$_2$]NO$_3$ in the *n*-heptane solution is advantageous to control the formation of silver(0) nanoparticles by changing the concentrations of the solutions, although the aggregation behavior has not been studied. A detailed characterization of this complex has also not been performed, although we have confirmed its formula and purity by elemental analysis and by ^{13}C NMR spectra. This complex is appreciably hydrophobic and we observed that it hardly incorporates water in *n*-hexane and therefore aggregation does not occur to a large extent.

For mesophases of silver(I) complexes, silver alkoxystilbazole complexes, including dinuclear complexes, have been extensively prepared, and the formation of both lyotropic and thermotropic liquid crystals has been studied.[4,5b] Con-

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cerning (amine)silver(I) complexes, the formation of thermotropic liquid crystal of $[Ag(n\text{-}C_nH_{2n+1}NH_2)_2]NO_3$ has been reported.[13] This complex shows a lamellar phase consisting of U-shaped (double-chained) molecules. For the *N*-alkyl-substituted (ethylenediamine)silver complexes, however, a detailed molecular structure and the molecular assembly in the liquid state have not been reported.

In the present study we have synthesized and investigated the molecular aggregation behavior of $[Ag(dod\text{-}en)_2]NO_3$ in comparison with $[Ag(hex\text{-}en)_2]NO_3$ and $[Ag(oct\text{-}en)_2]NO_3$ (the three complexes are represented by $[Ag(alkyl\text{-}en)_2]NO_3$ and found that the structure of $[Ag(dod\text{-}en)_2]NO_3$ is dinuclear from the X-ray crystallographic analysis and that a thermotropic liquid crystal is formed below 100 °C. We furthermore found that $[Ag(dod\text{-}en)_2]NO_3$ forms a lyotropic liquid crystal in *n*-heptane by incorporating small amounts of water. We performed the characterization of the lyotropic liquid crystals and the studies on the aggregation behavior of the complexes in water/organic mixed solvents. The aggregation behavior of the silver complexes in water/organic mixed solvent systems was mainly studied by measurement of the self-diffusion of the silver complexes.

Results and Discussion

X-ray Crystallographic Analysis

An ORTEP drawing of the complex is given in Figure 1; selected crystal data are given in the Exp. Sect. Four *N*-dodecylethylenediamine ligands coordinate to the two silver ions in the crystalline state; the coordination geometry around each silver ion is tetrahedral. The nitrate ions are arranged between the silver ions only as counterions. The diamine complexes previously reported tend to form ethylenediamine-bridged polymeric structures such as $[Ag(en)^+]_\infty$ and $[Ag(tn)^+]_\infty$ (tn = 1,3-propanediamine); in these systems, the coordination number of the silver ions is two.[14a,14c] In the present complex, on the other hand, polymerization does not occur and the dod-en ligands bridge two silver ions. The substitution of the diamine protons by alkyl chains in the silver complex obviously has a blocking effect on the polymerization. A related dinuclear silver complex, $[Ag_2H_2(en)_3]^{4+}$, has previously been identified by X-ray crystallographic analysis.[14b] In that case, the ethylenediamine bridges are cleaved by protonation to form a dinuclear complex where only one ethylenediamine ligand bridges two silver ions; the coordination number of the silver ion is two.

Although the present result reveals the structure in the crystalline state to be dinuclear, this complex should be appreciably dissociated into a mononuclear one in organic solvents, as will be described below, and thus we express the three silver complexes by the rational formula $[Ag(dod\text{-}en)_2]NO_3$ from here on.

Formation of Thermotropic Liquid Crystals

The formation of thermotropic liquid crystals was established by Differential Scanning Calorimetry (DSC) and polarizing microscopic observations for the neat complexes as follows. $[Ag(dod\text{-}en)_2]NO_3$ is crystalline below 59 °C and forms a mesophase over the temperature range 59−96 °C. Large and small endothermic peaks were observed in the DSC curves for the respective transitions. The transition data are listed in Table 1. This mesophase gave an oily streak texture accompanied by spontaneous homeotropic alignment, as shown in Figure 2; the oily streak means that the phase should be a smectic A one. Thus, X-ray diffraction measurement was carried out at 75 °C. The profile is

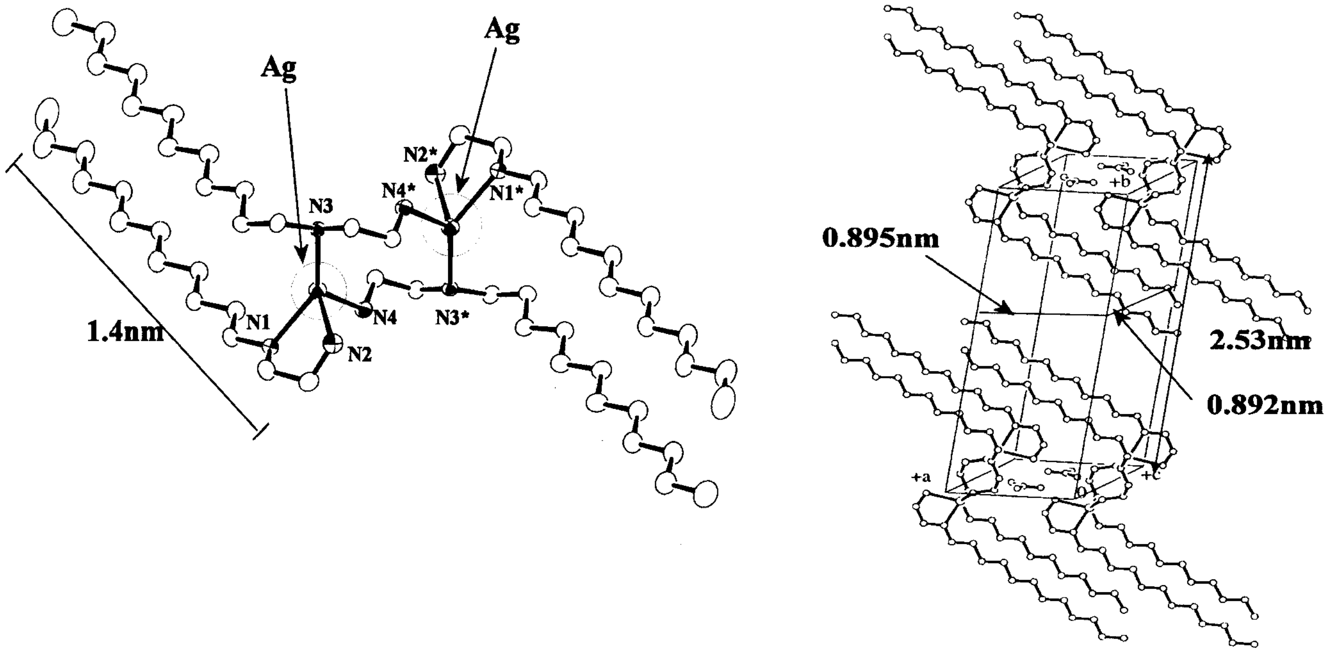

Figure 1. ORTEP diagram and atom-numbering system of $[Ag(dod\text{-}en)_2]No_3$

described in Figure 3 and the peak data are summarized in Table 2. As can be seen in this table, it shows a series of periodic reflections characteristic of a lamellar structure. Therefore, this mesophase could be characterized as a smectic A phase, as illustrated in Figure 4. According to the X-ray crystallographic analysis (Figure 1), twice the alkyl chain length is around 2.8 nm (1.4 nm × 2), which is close to the lamellar layer length (3.1 nm). As shown in Figure 4, if the contribution of the headgroup to the layer length is significant, the alkyl chain is possibly shortened in the mesophase.

Table 1. Thermal data for the phase transitions in the complexes $[Ag(dod\text{-}en)_2]NO_3$ and $[Ag(oct\text{-}en)_2]NO_3$[a]

	K $\rightleftarrows$ LC	LC $\rightleftarrows$ IL
$[Ag(dod\text{-}en)_2]NO_3$	$T = 59$; $\Delta H = 148$	$T = 96$; $\Delta H = 3.6$
$[Ag(oct\text{-}en)_2]NO_3$	$T = 48$; $\Delta H = 98$	$T = 67$; $\Delta H = 3.2$

[a] Temperatures are given in °C and ΔH values in $kJ\cdot mol^{-1}$; K = crystal, LC = liquid crystal, IL = isotropic liquid.

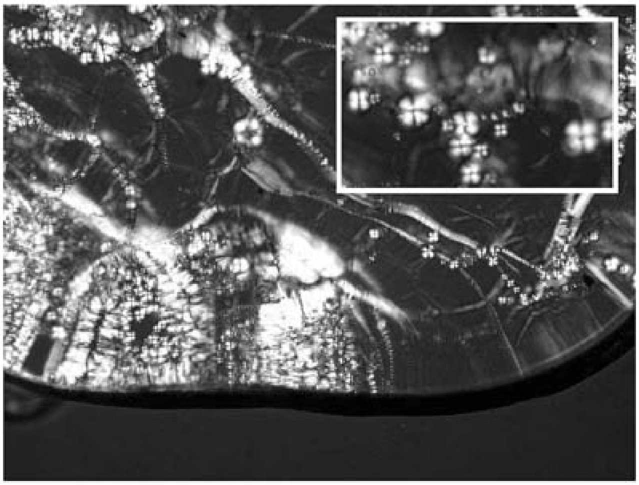

Figure 2. Optical textures observed for the neat $[Ag(dod\text{-}en)_2]NO_3$ complex at 75 °C

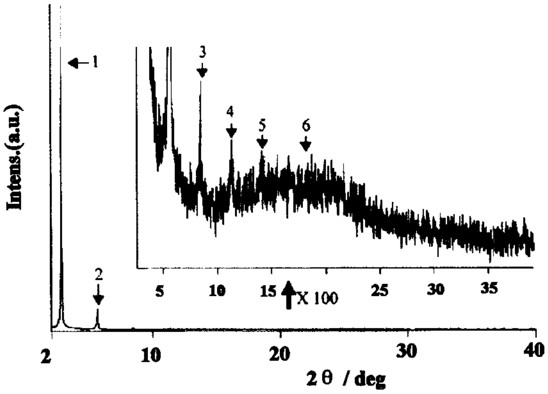

Figure 3. X-ray diffraction profile of the neat $[Ag(dod\text{-}en)_2]NO_3$ complex at 75 °C

Table 2. X-ray data for the $[Ag(dod\text{-}en)_2]NO_3$ thermotropic liquid crystal at 75 °C

Peak no.	Spacings [Å]		Miller indices (*hkl*)	Lattice constant [Å]
	Observed	Calculated		
1	31.1	31.3	(001)	
2	15.7	15.6	(002)	
3	10.4	10.4	(003)	S_A; $c = 31.3$
4	7.81	7.82	(004)	
5	6.27	6.25	(005)	
6	ca. 4.7	–	[a]	

[a] Halo of molten alkyl chains.

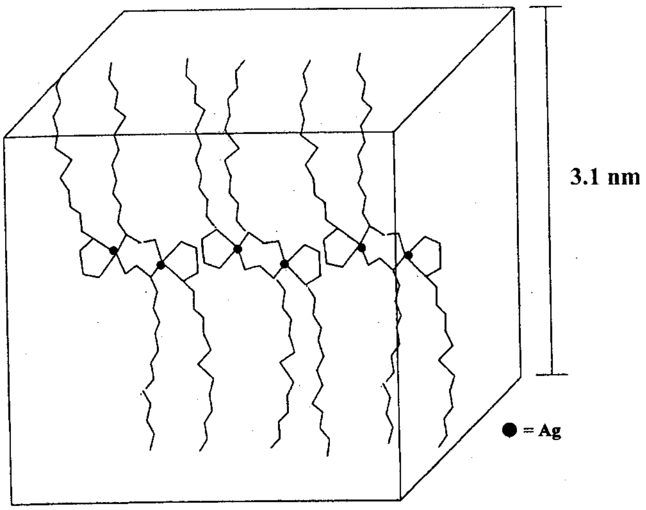

Figure 4. Schematic representation of the smectic A phase for the $[Ag(dod\text{-}en)_2]NO_3$ complex

$[Ag(oct\text{-}en)_2]NO_3$ also forms thermotropic liquid crystals but the formation is weaker than that for $[Ag(dod\text{-}en)_2]NO_3$. The thermal data are listed in Table 1; no liquid-crystalline phase was detected for $[Ag(hex\text{-}en)_2]NO_3$.

Solubility of $[Ag(alkyl\text{-}en)_2]NO_3$ in Organic Solvents and Formation of a Lyotropic Liquid Crystal of $[Ag(dod\text{-}en)_2]NO_3$ in Water/*n*-Heptane

$[Ag(dod\text{-}en)_2]NO_3$ is soluble in only a few solvents. At 25 °C this complex is soluble [> 10% (wt/v)] in dichloromethane, and sparingly soluble [a few % (wt/v)] in methanol and ethanol. The $[Ag(oct\text{-}en)_2]NO_3$ complex, on the other hand, is readily soluble in DMF, acetone, benzene, and 1,4-dioxane, and sparingly soluble in dichloromethane, ethyl acetate, diethyl ether, and chloroform. This complex is not stable in methanol and ethanol. The most hydrophilic complex, $[Ag(hex\text{-}en)_2]NO_3$, is readily soluble in many solvents, such as water, DMF, methanol, ethanol, acetone, dichloromethane, ethyl acetate, and 1,4-dioxane. As this complex seems to have similar properties to common surfactants, a detailed study of its aggregation behavior has not been performed.

It is noteworthy that the solubility of $[Ag(dod\text{-}en)_2]NO_3$ in *n*-heptane and 1,4-dioxane and that of $[Ag(oct\text{-}en)_2]NO_3$ in *n*-heptane are largely enhanced by the presence of small amounts of water. Such a solubility phenomenon does not occur for $[Ag(hex\text{-}en)_2]NO_3$. This solubility enhancement suggests the formation of aggregates of the metal complexes surrounding a water "pool", where the hydrophilic sites of the silver complex ions would be collected. Figure 5 shows three-component phase diagrams of the $[Ag(dod\text{-}en)_2]NO_3$ and $[Ag(oct\text{-}en)_2]NO_3$ systems for the formation of transparent and homogeneous solutions in water/1,4-dioxane and water/*n*-heptane mixed solvent systems. It is interesting to compare the preferable interaction between the silver complexes and solvents with those of our previous studies for $[ZnCl_2(oct\text{-}en)_2]$, $[CdCl_2(oct\text{-}en)_2]$, and $[Pd(oct\text{-}en)_2]Cl_2$.[11,15] The zinc complex of a weak electrolyte and the palladium complex of a strong electrolyte are extensively dissolved in water/benzene and water/chloroform mixed solvents, respectively, to form large aggregates (microemulsions). The higher affinity of the $[Ag(dod\text{-}en)_2]NO_3$ and $[Ag(oct\text{-}en)_2]NO_3$ complexes for *n*-heptane than for more polar solvents such as benzene and chloroform indicates their higher hydrophobicity compared to $[ZnCl_2(oct\text{-}en)_2]$ and $[CdCl_2(oct\text{-}en)_2]$ despite their being strong electrolytes. The $[Ag(hexd\text{-}en)_2]NO_3$ complex previously reported is soluble in neat *n*-heptane without water[12] and does not incorporate even small amounts of water in *n*-heptane. The result of the $[Ag(dod\text{-}en)_2]NO_3$/water/*n*-heptane system (Figure 5b) shows that the transparent and homogeneous phase is especially large in the $[Ag(dod\text{-}en)_2]NO_3$ complex; this feature reflects the moderate hydrophile/lipophile balance of this complex. The dinuclear complex is almost completely changed to the mononuclear complex in solution, as will be described below. This structural change may also cause the unique solubility phenomena.

We also found a very narrow phase region of lyotropic liquid crystals in the $[Ag(dod\text{-}en)_2]NO_3$/water/*n*-heptane system (Figure 5b). The structural characterization and studies of the physical properties are discussed below.

Vapor-Pressure Depression, Electric Conductivity, and Mass Spectrometric Studies for the $[Ag(dod\text{-}en)_2]NO_3$ Complex in Some Organic Solvents

We measured the physical properties of solutions to determine the aggregation behavior of the $[Ag(dod\text{-}en)_2]NO_3$ complex. The apparent molecular weight (MW_{app}) of the complex was estimated from the vapor-pressure depression Δp [which is proportional to ΔT of Equation (2) in the Exp. Sect.] of the solutions (methanol, dichloromethane, and *n*-hexane systems) as a function of the silver complex concentrations (m; $g{\cdot}kg^{-1}$). As a first approximation, we estimated the MW_{app} values by assuming that the silver complex is a nonelectrolyte. The ΔT vs. m plots are slightly curved for dichloromethane and methanol solutions. The MW_{app}/MW ratios (R_{MW}) obtained for $[Ag(dod\text{-}en)_2]NO_3$ (626.72) were 1.5−2.5 in dichloromethane $\{[Ag(dod\text{-}en)_2]NO_3 =$

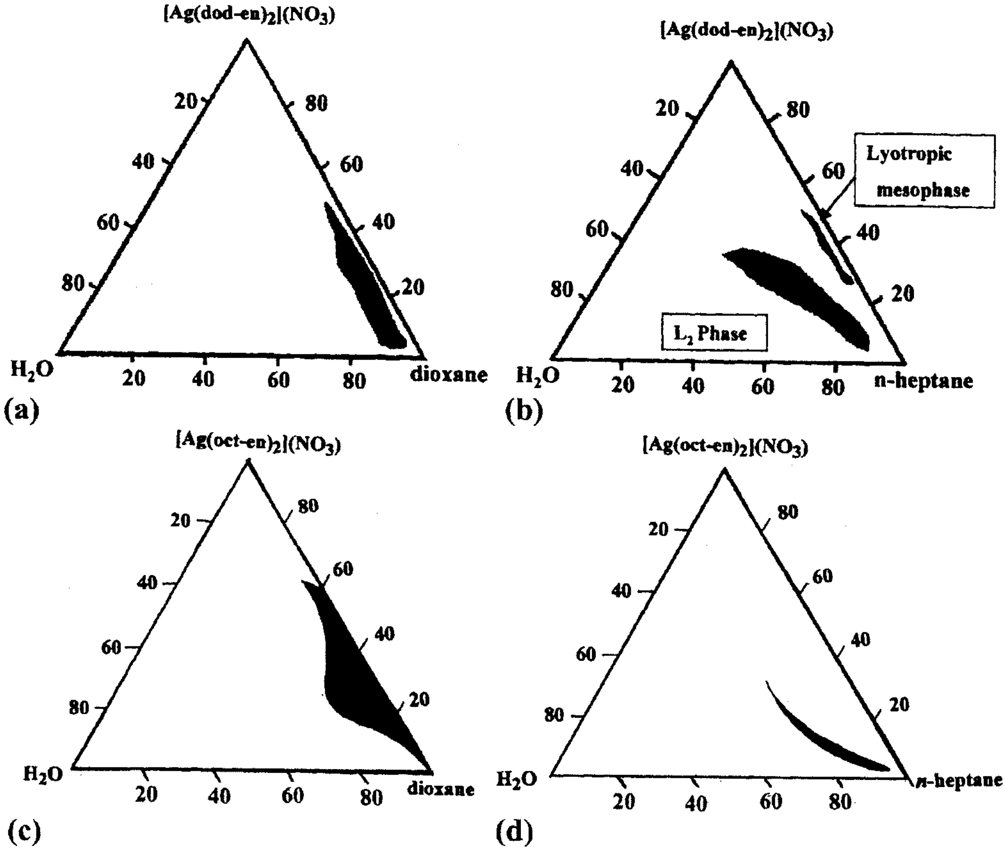

Figure 5. (a) Partial mass (wt.-%) ternary phase diagrams for the transparent and homogeneous solutions in the $[Ag(dod\text{-}en)_2]NO_3$/1,4-dioxane/water system at 30 °C; (b) partial mass (wt.-%) ternary phase diagrams for the homogeneous solutions in the $[Ag(dod\text{-}en)_2]NO_3$/*n*-heptane/water system at 30 °C; L_2 is water in oil phase

0.19−1.29 mol·kg^{-1}}, 0.8−1.1 in methanol {[Ag(dod-en)$_2$]NO$_3$ = 0.04−0.51 mol kg^{-1}}, and 15.5 in *n*-heptane {[Ag(dod-en)$_2$]NO$_3$ = 0.97−1.32 mol kg^{-1}}, where a small amount of water is present and the phase is a lyotropic liquid crystal. The obtained R_{MW} values are < 2 under some conditions. This is due to two factors, one of which is the dissociation of the salt into the silver complex ion and the nitrate ion and the other is the dissociation of the dinuclear complex into the mononuclear one. Concerning the former factor, we measured electric conductivities of the [Ag(dod-en)$_2$]NO$_3$ methanol solutions in the concentration range 0.01−0.12 mol·dm^{-3}. At lower concentrations, the molar electric conductivities depend on the concentration and almost obey the Onsager equation assuming a 1:1 electrolyte (Supporting Information; Figure S1a). As the dependence of the electric conductivity on the concentration is larger than that of the self-diffusion, we estimated the limiting molar conductivity of the silver complex ion in order to obtain a more accurate value by use of the self-diffusion coefficient of the silver complex ion according to the Nernst equation.[16] [The limiting molar conductivity (Λ^0) of the silver complex thus obtained was 8.7×10^{-3} S·m^2·mol^{-1} by using $\lambda_0 = 6.1 \times 10^{-3}$ S·m^2·mol^{-1} for the nitrate ion in methanol at 25 °C; this Λ^0 value is reasonable as an extrapolated value.] This result indicates that at lower concentrations in methanol this complex would be completely dissociated into [Ag(dod-en)$_2$]$^+$ and NO$_3^-$. At higher concentrations, where the vapor-pressure depression was measured, the Onsager plot is largely curved and the ionic interactions become stronger and more complicated. The R_{MW} value of 0.8−1.0 obtained from the VPO measurement in this concentration range means that the interaction between [Ag(dod-en)$_2$]$^+$ and NO$_3^-$ is stronger than that at lower concentrations. In methanol, the electric conductivities (κ) are around 0.1−0.5 S·m^{-1} at 0.01−0.2 mol·dm^{-3}, whereas in dichloromethane they are around 0.1−0.2 S·m^{-1} at 0.12−0.90 mol·dm^{-3} (Supporting Information; Figure S1b). The significantly smaller electric conductivities in dichloromethane mean that the dissociation of the silver complex into the monomer or into the ions occurs to a lesser extent in dichloromethane than in methanol. This trend is consistent with the result of the vapor-pressure depression.

In order to determine the nature of the species in solution, we also measured nano-ESI mass spectra of the silver dod-en complexes in methanol and in dichloromethane. A typical spectrum is shown in Figure 6. The percentages of the peak areas of [Ag$_2$(dod-en)$_4$]NO$_3^+$ (*m*/*z* = 1188.82, ^{12}C$_{56}{}^{1}$H$_{128}{}^{107}$Ag$_2{}^{14}$N$_9{}^{16}$O$_3$)/[Ag$_2$(dod-en)$_3$]NO$_3^+$ (*m*/*z* = 960.57, ^{12}C$_{42}{}^{1}$H$_{96}{}^{107}$Ag$_2{}^{14}$N$_7{}^{16}$O$_3$)/[Ag(dod-en)$_2$]$^+$ (*m*/*z* = 563.42, ^{12}C$_{28}{}^{1}$H$_{64}{}^{107}$Ag^{14}N$_4$) were as follows: 2.4%/4.6%/93% for a 0.048 mol·dm^{-3} methanol solution, 7.2%/7.2%/85.6% for a 0.064 mol·dm^{-3} dichloromethane solution, and 10.2%/15.6%/74.2% for a 0.16 mol·dm^{-3} dichloromethane solution. Although the percentages obtained do not necessarily reflect the distribution of each species in solution due to complicated ionization processes, this result does not conflict with the view that the dinuclear complex found in the crystalline state would be appreciably dissociated into the mononuclear complex even at moderate concentrations in organic solvents. A similar formation of mixed mononuclear and dinuclear ethylenediamine (en) complexes of silver such as Ag(en)$^+$, Ag$_2$(en)$^{2+}$, Ag(en)$_2^+$, and Ag$_2$(en)$_2^{2+}$ has been previously reported in water.[17] For the en complex, a

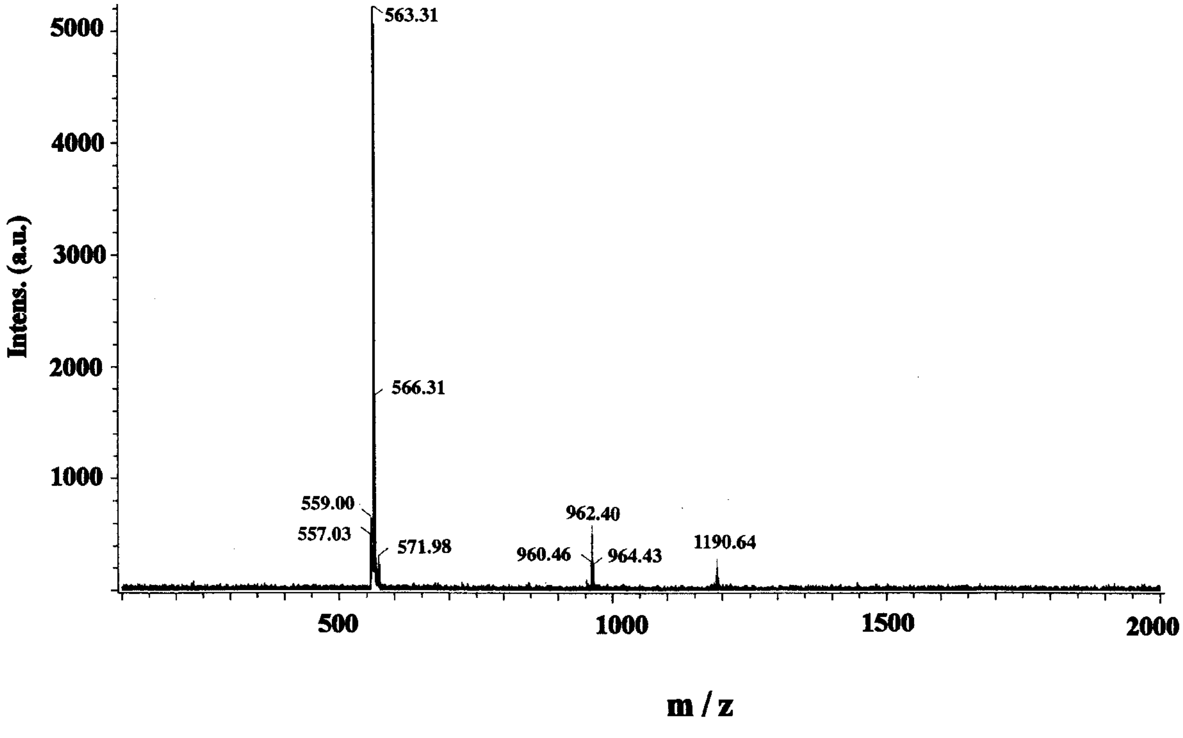

Figure 6. Nano-ESI-TOF mass spectrum of 0.16 M [Ag$_x$(dod-en)$_y$](NO$_3$)$_z$ complexes in dichloromethane

polynuclear structure in the solid state decomposes into the dinuclear and mononuclear complexes in water.

Observation of the Lyotropic Liquid Crystal by Micrograph for the [Ag(dod-en)$_2$]NO$_3$/Water/n-Heptane System

Figure 7 shows a photomicrograph of the lyotropic mesophase in [Ag(dod-en)$_2$]NO$_3$/water/*n*-heptane mixtures at room temperature. It gave a schlieren texture containing both two and four brushes, which is characteristic of a nematic phase.[18] Hence, this lyotropic mesophase can be identified as a nematic phase. As the molecular structure of this dinuclear and double-chained complex is favorable to form thermotropic liquid crystals at temperatures higher than room temperature, this molecule furthermore loses order in one dimension in the water-containing *n*-heptane to form a nematic lyotropic liquid crystal. The presence of small amounts of water plays an important role in the stabilization of the liquid-crystalline structure by assembling the headgroup of the silver complex and by organizing the supramolecules. This difference in the superstructure of this complex between the neat state and the solution state can be attributed to a loss of molecular orderings in the assemblies by the presence of *n*-heptane. It is notable that the dinuclear complex in the crystalline state would be significantly dissociated into a monomer in organic solvents as described above. The presence of small amounts of water will promote this dissociation. Thus, the lyotropic liquid crystal may be mainly composed of a mononuclear double-chained [Ag(dod-en)$_2$]NO$_3$ complex. As the dissociation of the nitrate ions from the silver salt in the water/*n*-heptane system may be slight because of a large excess of *n*-heptane over water in the lyotropic liquid crystalline phase, the R_{MW} value (15.5) obtained from the vapor-pressure depression in the water/*n*-heptane system will be close to the aggregation number of [Ag(dod-en)$_2$]NO$_3$ ion-pairs.

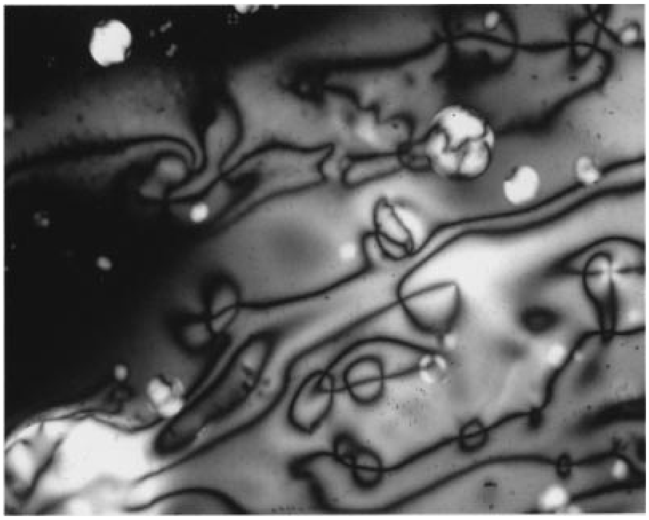

Figure 7. Optical texture observed for the lyotropic liquid crystal of the [Ag(dod-en)$_2$]NO$_3$/water/*n*-heptane system

^{2}H NMR Spectra and Small-Angle X-ray Scattering (SAXS) for the Lyotropic Mesophase

The lyotropic liquid crystal forms in very narrow composition and temperature ranges, and the small amounts of water play an important role in forming the mesophase. In order to monitor the formation of lyotropic mesophases containing water from a microscopic viewpoint, we expected the ^{2}H NMR spectra to provide useful information. As the water content in the present lyotropic mesophase is small (W_0 = [water]/[silver complex] < 2), most water molecules can be regarded as water of hydration. Thus, we can directly monitor the nature of the aggregates in the ne-

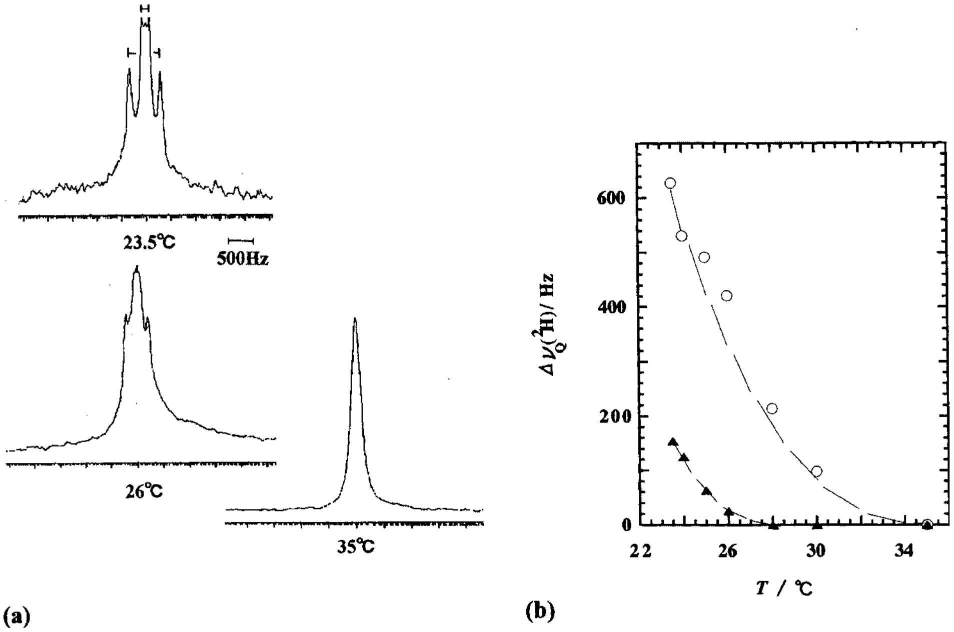

Figure 8. (a) ^{2}H NMR spectra of the trace water in the [Ag(dod-en)$_2$]NO$_3$/water/*n*-heptane system as a function of temperature (W_0 = 1.7 and m = 1.2 mol kg^{-1}); (b) change in the ^{2}H$_2$O quadrupole splitting for the two kinds of liquid crystalline peaks

matic lyotropic mesophase by ^{2}H NMR spectroscopy. Figure 8a shows the ^{2}H NMR spectra of trace water in the $[Ag(dod\text{-}en)_2]NO_3$/water/*n*-heptane system as a function of temperature. The ^{2}H NMR quadrupole splittings of the liquid-crystalline spectra as a function of temperature are shown in Figure 8b. The absolute values of the quadrupole splittings are consistent with a nematic phase.[19] This figure indicates the presence of two kinds of hydration modes. As the exchange of the hydration water between the two states is slow enough on the NMR timescale, the two kinds of water would reflect those of molecular assemblies.

We observed one SAXS peak at $2\theta = 1.4°$ ($d = 6.3$ nm, which is nearly twice the bilayer thickness of 3.1 nm) in the same lyotropic mesophase as used for the ^{2}H NMR spectra; no clear peak was observed in the SAXS spectrum for the isotropic microemulsions (L_2 phase in Figure 5b). Therefore, it is possible that the smaller ^{2}H NMR splitting arises from hydration of the domains close to the isotropic microemulsions.

The narrow temperature and concentration ranges of the nematic lyotropic mesophase mean that the mesophase could form because of the delicate balance of the hydrophilicity/lipophilicity of the silver complex and the selective hydration in *n*-heptane solution.

Self-Diffusion Studies for the Aggregation of $[Ag(dod\text{-}en)_2]NO_3$ in Solution

The self-diffusion coefficients of the solvent and solute were calculated to monitor the extent of aggregation, especially in mixed-component systems. We thus measured the diffusion coefficients of the $[Ag(dod\text{-}en)_2]NO_3$ complex and the solvents in water/*n*-heptane and dichloromethane in comparison with those in methanol where aggregation hardly occurs.

Figure 9 shows the results for water and the silver complex as a function of the silver complex concentrations. In the water/*n*-heptane system, the solute concentration is expressed for the neat *n*-heptane solvent (neglecting small amounts of water). In Figure 9a, the diffusion coefficients in methanol could be obtained only in a very narrow concentration range due to solubility limitations; those at low concentration are regarded as those of the monomer.

The diffusion coefficients obtained can be interpreted on the basis of the Stokes–Einstein equation at infinite dilution according to Equation (1), where R is the Stokes radius for the monomer, k the Boltzmann constant, T the absolute temperature, and η_0 the viscosity of the solvent.

$$R = kT/6\pi\eta_0 D_0 \qquad (1)$$

We can estimate the Stokes radius for the silver complex in dilute methanol solution or in dichloromethane by an extrapolation of the diffusion coefficients to an infinite dilution in Figure 9a; we obtain a D_0 value in methanol of 6.8×10^{-10} $m^2{\cdot}s^{-1}$ and in dichloromethane of 8.4×10^{-10} $m^2{\cdot}s^{-1}$. By using an η_0 value for methanol of 0.542 mPa s[20] and a value for dichloromethane of 0.41 mPa·s at 25 °C[20] the R values are 0.67 nm and 0.71 nm, respectively. The larger size in dichloromethane is consistent with the results of the vapor-pressure depression and mass spectrometric measurements. The significant decrease in the diffusion coefficients at higher concentrations indicates the extensive aggregation.[21]

As deuterated *n*-heptane is unobtainable, we measured the diffusion coefficients of the silver complex in water/*n*-heptane solutions indirectly as will be described in the Exp. Sect. The measurements of diffusion coefficients in the *n*-heptane/water system were performed in both the water in oil (w/o) microemulsion phase (larger W_0 regions) and the lyotropic liquid-crystalline phase (smaller W_0 regions) (Figure 9b). We can furthermore estimate the Stokes radius for the metal complex in *n*-heptane ($D_0 = 8.7 \times 10^{-11}$ $m^2{\cdot}s^{-1}$)

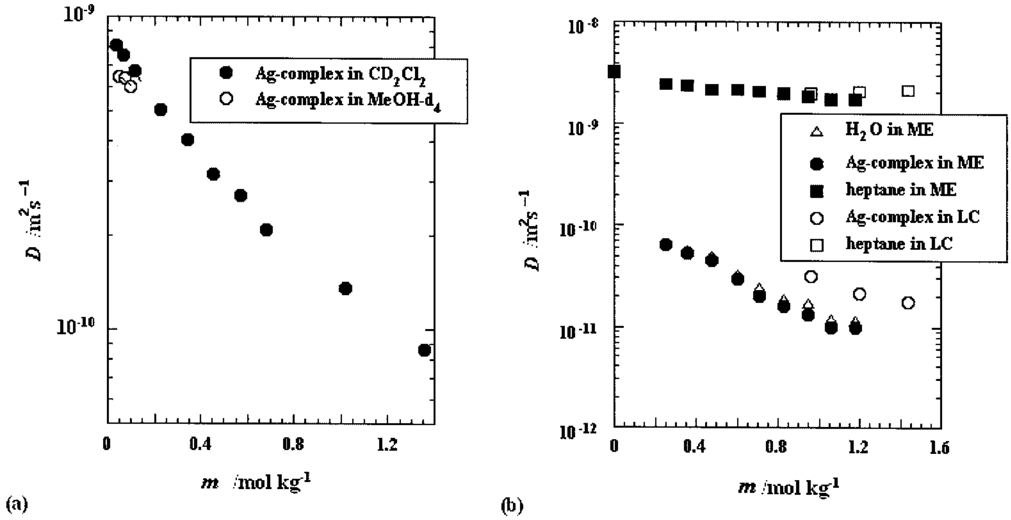

Figure 9. (a) Diffusion coefficients for the $[Ag(dod\text{-}en)_2]NO_3$ complex in [D4]MeOH and [D2]dichloromethane as a function of the mononuclear silver complex concentration; (b) diffusion coefficients for water, *n*-heptane, and the complex in the $[Ag(dod\text{-}en)_2](NO_3)_2$/*n*-heptane/water system [in the microemulsion (ME) and liquid crystal (LC) systems] as a function of the mononuclear silver complex concentrations ($W_0 = 30$ in the ME system and $W_0 = 1.7$ in the LC system)

by neglecting small amounts of water. (η_0 = 0.397 mPa·s for *n*-heptane) The obtained value of 6.4 nm is appreciably larger than those in methanol and dichloromethane. This result clearly indicates that the silver complex is readily dissolved in *n*-heptane only when large aggregates are formed by incorporation of water.

We can see the other two characteristic features in Figure 9b. Firstly, the diffusion coefficient of water is appreciably smaller than that of *n*-heptane and is slightly larger than that of the silver complex. Secondly, the diffusion coefficients of the silver complex in the liquid-crystalline region are significantly larger and those of solvent *n*-heptane are also slightly larger than those in the microemulsion systems. The first feature in the water diffusion means that water tends to move together with the silver complex and is motionally restricted to a large extent. This indicates the formation of reversed micelles or W/O microemulsions. The second feature is consistent with a nematic liquid crystal characterized by a polarizing microscope, since the viscosity of the nematic lyotropic liquid crystal will be lower than that of the isotropic phase of the same surfactant concentration. The water content is appreciably smaller in the lyotropic liquid crystal than in the W/O microemulsion state in spite of the slightly larger concentration of the silver complex in the former state. This difference of the silver complex concentration will tend to make the diffusion coefficient in the liquid crystal phase smaller than that in the W/O microemulsion system. However, the result obtained is opposite to this prediction, which may reflect the lower viscosity of the nematic-type liquid crystal. Although *n*-heptane seems to be an unfavorable solvent to form lyotropic liquid crystals due to a lower molecular rigidity and a lower polarity, the rigid structure of the present complex and the small amounts of incorporated water may play important roles in forming the anisotropic superstructure.

In order to see the water effect on the aggregation, we furthermore measured the diffusion coefficients of the silver complexes depending on the water content in the 1,4-dioxane and *n*-heptane systems. Figure 10a shows that in the 1,4-dioxane/water system the diffusion coefficients of $[Ag(hex\text{-}en)_2]^+$, $[Ag(oct\text{-}en)_2]^+$, and $[Ag(dod\text{-}en)_2]^+$ slightly increase with increasing water content. In this figure, the silver complex concentration is expressed for the neat 1,4-dioxane solvent. The diffusion coefficients increase probably due to the dilution of the solution with an addition of water. The dod-en complex is dissolved in 1,4-dioxane in the presence of water and the effect of water on the aggregation of $[Ag(dod\text{-}en)_2]^+$ is only slight, contrary to the dilution effect. This result means that water assists the dissolution of this complex in 1,4-dioxane by the formation of aggregates.

This effect of water on the diffusion appears more clearly in the *n*-heptane system, as shown in Figure 10b, where it is characteristic that addition of water decreases the diffusion coefficients of the $[Ag(dod\text{-}en)_2]^+$ complex and of both solvents. In this system, water clusters move together with the silver complex aggregates and assist the aggregation of the silver complex. As the diffusion of *n*-heptane is also decreased by addition of water, water will assist the aggregation of the silver complex to form a W/O microemulsion more than in the 1,4-dioxane system. The effect of the aggregation on the diffusion would be larger than the opposite effect on aggregation due to dilution with an increase in the water content, and thus the diffusion is decreased by addition of water.

In conclusion, we have synthesized and characterized new amphiphilic alkylethylenediamine dinuclear silver complexes. Although the ligand is regarded as a simple and common type, a unique rigid structure of the tetrakis(dodecyl)-substituted complex gives rise to a formation of therm-

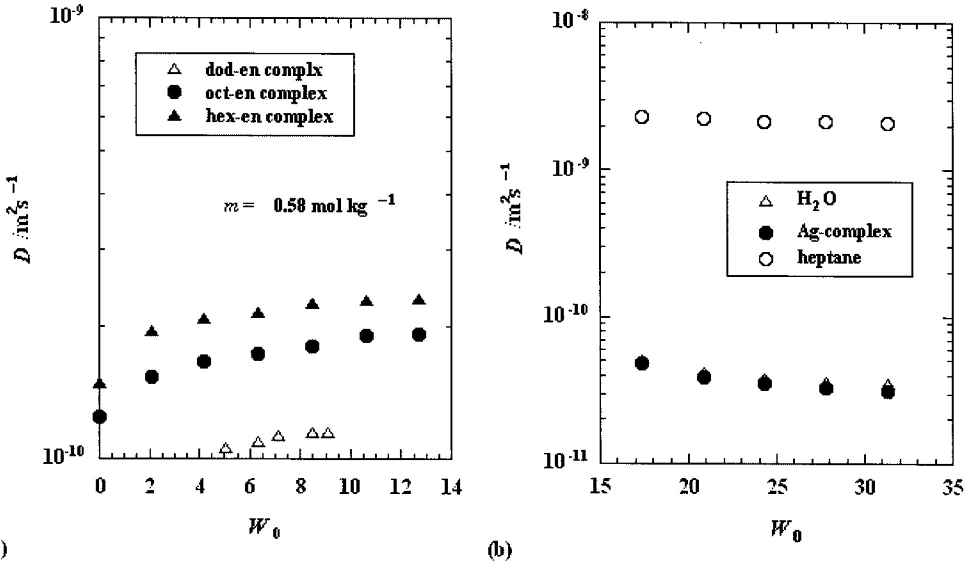

Figure 10. (a) Diffusion coefficients of $[Ag(hex\text{-}en)_2]^+$, $[Ag(oct\text{-}en)_2]^+$, and $[Ag(dod\text{-}en)_2]^+$ in water-containing [D$_8$]1,4-dioxane systems as a function of the water content; (b) diffusion coefficients of $[Ag(dod\text{-}en)_2]^+$ and the solvents in the water-containing *n*-heptane system as a function of the water content

otropic liquid crystals. Small amounts of water play an important role in concentrating the silver headgroup in the nanosized water pools and thereby aligning the assemblies of the silver complex for the superstructure.

Experimental Section

Materials: *N*-Hexylethylenediamine, *N*-octylethylenediamine, and *N*-dodecylethylenediamine were prepared according to reported procedures.[11a,11b] The silver complexes were synthesized according to a similar procedure as described for the *N*-hexadecylethylenediamine complex but the crystallization from the reaction mixtures was performed by the addition of cyclohexane to a methanol solution. The molecular formula and purity were determined by elemental analyses and ^{13}C NMR spectroscopy. The yields after recrystallization were about 80%. [Ag(hex-en)$_2$]NO$_3$: $C_{16}H_{40}AgN_5O_3$ (458.41): calcd. C 41.92, H 8.80, N 15.28; found C 41.69, H 8.80, N 15.17. [Ag(oct-en)$_2$]NO$_3$: $C_{20}H_{48}AgN_5O_3$ (514.50): calcd. C 46.69, H 9.40, N 13.61; found C 46.64, H 9.31, N 13.47. [Ag(dod-en)$_2$]NO$_3$: $C_{28}H_{64}AgN_5O_3$ (626.7): calcd. C 53.66, H 10.29, N 11.17; found C 53.92, H 10.15, N 11.20. Chloroform, dichloromethane, methanol, and 1,4-dioxane were guaranteed grades supplied by Wako Pure Chemical Industries. Chloroform was purified as previously reported.[11d] Dichloromethane was dried with calcium chloride and then distilled; the water content was $< 1 \times 10^{-3}$ %. Methanol and 1,4-dioxane were distilled once before use. Water was distilled twice. The deuterated solvents (D_2O, [D$_4$]MeOH, [D$_2$]dichloromethane, and [D$_8$]1,4-dioxane) were supplied by Merck Co.

Single-Crystal X-ray Diffraction Analysis for [Ag(dod-en)$_2$]NO$_3$: A colorless plate (0.30 × 0.25 × 0.05 mm) was fixed on the top of a glass fiber with Paraton N oil, and 3854 reflections ($6° < 2\theta < 52°$) were measured with a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo-K_α radiation at −70 °C. An absorption correction by a spherical multiscan method was applied ($\mu = 6.1$ cm^{-1}). The structure was solved by direct methods using the program SIR92[22] and was refined with full-matrix least-squares techniques to $R = 0.061$ and $R_w = 0.066$ for 4517 independent reflections with $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms, located in ideal positions, were not refined. All calculations were performed with a Silicon Graphics O2 Station with the teXsan program system.[23] The crystal data and experimental details are summarized in Table 3. CCDC-244806 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Observations of the Structures of the Liquid Crystals: Thermotropic and lyotropic mesomorphisms were established using the samples exhibiting satisfactory elemental analysis data of C, H and N. For the thermotropic mesomorphism, the phase-transition phenomenon was observed using a polarizing microscope (Olympus BH2), equipped with a heating plate controlled by a thermo-regulator (Mettler FP80 hot stage, Mettler FP82 central processor), and measured by a differential scanning calorimeter (Shimadzu DSC-50). The X-ray diffraction measurement for the thermotropic liquid crystal was performed with Cu-K_α radiation (Rigaku RAD) equipped with a hand-made heating plate[24] controlled by a thermo-regulator. For the lyotropic system, the mesophase at room temperature was characterized by the polarizing microscope, ^2H_2O NMR spectroscopy, and small-angle X-ray scattering ($0.5° < 2\theta < 5°$) with Cu-K_α radiation (Rigaku RAD), where a plastic cell of 3 mm thickness with mica windows was used and the intensity distribution was measured with a position-sensitive proportional counter (PSPC).

Table 1. Crystallographic and experimental data for [Ag(dod-en)$_2$]NO$_3$

Empirical formula	$C_{56}H_{128}Ag_2N_{10}O_6$
Formula mass	1253.43
Crystal system	triclinic
Crystal size [mm]	0.30 × 0.25 × 0.05
Space group	$P\bar{1}$ (no. 2)
a [Å]	8.9479(2)
b [Å]	25.318(3)
c [Å]	8.9207(2)
α [°]	80.33(2)
β [°]	118.51(2)
γ [°]	95.64(2)
V [Å^3]	1750.2(4)
Z	1
T [°C]	70
D_{calcd} [g cm^{-3}]	1.189
Abs coeff [cm^{-1}]	6.06
Diffractometer	Rigaku/MSC Mercury CCD
ω oscillation range [°]	70.0−100.0
Exposure rate [s/°]	120
Data images	1440
2θ range [°]	$6 < 2\theta < 52$
No. of unique data	6135
No. of obsd. data	4517 [$I > 2\sigma(I)$]
No. of variables	335
Data/parameters	13.48
R[a]	0.061
R_w[a]	0.066
GOF[b]	1.50

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ [$w = 1/\sigma^2(F_o)$]. [b] GOF = $[\Sigma w(|F_o| - |F_c|)^2/[N_o - N_p]]^{1/2}$ (N_o = number of data, N_p = number of variables).

NMR Measurements: The aggregation behavior in solution was monitored by NMR spectroscopy. The ^2H NMR spectra were obtained with a JEOL JNM EX-270 FT NMR spectrometer operating at 41.5 MHz for 20% enriched ^2H_2O, small amounts of which are contained in the lyotropic liquid crystalline system. The self-diffusion coefficients were measured by the NMR PFG (Pulsed Field Gradient) technique.[25] The measurements were performed with a JEOL FX-90 spectrometer operating at 90 MHz for ^1H. The spectrometer was equipped with an apparatus that produced a field gradient in the range 0.3−1.0 T/m. For water, the change in the intensity of the ^{1}HDO signal was monitored. For the surfactant, the intensity of the methylene ^1H signals of the alkyl chains was monitored. In the *n*-heptane (deuterated reagent was not supplied) system, the ^1H peaks of the silver complex were completely covered by those of the solvent. However, the attenuation of the spin-echo amplitude after the Fourier transformation of the solvent peaks decayed much more rapidly with a change in the duration (δ) of the applied gradient pulses ($0.2 < \delta < 5$ ms) than that of the silver complex. Thus, we could obtain the diffusion coefficients of the silver complexes even in the *n*-heptane system. The accuracy of the measured diffusion coefficients is estimated to be better than ±5%, although that for the silver complex in the *n*-heptane system is somewhat worse.

Other Measurements: The vapor-pressure depressions for the solutions of methanol, dichloromethane, and *n*-heptane containing small amounts of water[26] were measured with a Knauer Vapor Pressure Osmometer (VPO) at 45 °C. The magnitude of the depression is proportional to the difference in temperatures (ΔT) between a solvent-wetted thermistor and a solution-wetted one. If the dissociation of the counterion is negligible, Equation (2) can be applied, where k is a constant depending on the solvent and the apparatus used, M_1 the apparent molecular weight of the solute, and m' the solute concentration in g·kg^{-1}.

$$\Delta T = km'/M_1 \tag{2}$$

The k value was determined from benzil solutions. The electric conductivities of the methanol and dichloromethane solutions were measured using an admittance linear bridge (FUSO 362A) operated at 1 kHz. The mass spectra of the silver dod-en complexes in methanol and dichloromethane were measured with a Jeol JMS-T100 (AccuTOF) ESI-TOF mass spectrometer.

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