

Novel Class of Ionic Metallomesogens without Organic Ligands: Thermotropic Liquid-Crystalline Behavior of Tetrachlorometalate Salts and Distinct Polymorphic Transition in Smectic A Phases

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The thermotropic liquid-crystalline behavior of the metal complex salts $[(C_{18}H_{37})(CH_3)_3N]_2[MCl_4]$ and $[(C_{18}H_{37})_2(CH_3)_2N]_2[MCl_4]$ ($M = Co, Ni, Cu, Zn, Cd$) was evaluated by differential scanning calorimetry, polarizing optical microscopy, X-ray diffraction, and electronic absorption as well as by Raman spectroscopy. Introduction of divalent metal ions into the cationic amphiphiles was found to result in enhancement of their thermal properties. Although the parent tetraalkylammonium chlorides showed no liquid-crystalline phase (or indistinct transition behavior), the derived tetrachlorometalate salts exhibited a stable liquid-crystalline phase and simple phase transition behavior. For instance, the tetrachlorocobaltate salt, $[(C_{18}H_{37})_2(CH_3)_2N]_2[CoCl_4]$, showed a smectic A (S_A) phase in an extremely wide temperature range from 45 to 155 °C on heating. In the S_A phase, the complexes were confirmed to form a layered self-assembly that is built up from alternating layers of tetrahedral $[MCl_4]^{2-}$ ions and flexible alkyl segments. Furthermore, distinct polymorphism in the S_A phase was observed for several tetrachlorometalate salts, which differs essentially from the S_A-S_A transition described in the usual rodlike liquid crystals.

Introduction

In recent years, metal-containing thin film assemblies have attracted much attention for their characteristics such as electronic conductivity, semiconductivity, superconductivity, ferroelectricity, and magnetism. In particular, layered thin films with two-dimensional arrays of metal atoms are potential materials for electrooptic applications in sensors and memories.¹ Generally, such layered thin films are artificially prepared from inorganic or organic crystalline materials by a variety of techniques (such as sputtering, laser ablation, chemical vapor deposition, the Langmuir–Blodgett technique, and sol–gel processing).^{1f,g,2} On the other hand, spontaneous formation of two-dimensional

layered structures can be accomplished by introduction of divalent metal ions into inorganic solids. For instance, K_2NiF_4 provides a typical example of a layered crystalline material, and the related cupric compounds with two-dimensional CuO_2 sheet structures have been used extensively as oxide superconductors.^{1a,3} In the area of organic solids, the formation of ordered molecular systems with two-dimensional features can be achieved most commonly for single crystals of coordination compounds containing metal atoms bonded to organic ligands via heteroatoms.^{1c,4}

There is currently considerable interest in mixed organic/inorganic materials in which features of the organic and inorganic components complement each other, leading to new solid-state structures and materials with composite or even new properties.^{1d,5} Divalent

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metal complexes having structurally simple amphiphiles are one of the most representative examples of these organic/inorganic materials. For instance, metal organophosphonates,^{2c,6} such as $M(O_3PR) \cdot H_2O$ ($M = Mg, Mn, Zn, Ca, Cd$; $R = n$ -alkyl, aryl group) and $M(HO_3PR)_2$ ($M = Ca$), and bis(alkylammonium) tetrahalogenometalate salts,^{3,7} such as $(RNH_3)_2[MX_4]$ ($R = n$ -alkyl; $M = Cu, Mn, Cd, Fe, Pd, Co, Zn$; $X = Cl, Br$), show two-dimensional layered structures of divalent metal ions with the aid of organic amphiphilic components. Such hybrid materials are favorable from the viewpoint of modification of the layer structure, because their structures are directed by the choice of metal and the nature of their interlayer regions depends on the flexible organic components. Even in the hybrid materials, however, there is a problem in the preparation of metal-containing thin films with two-dimensional domains. Because most of them are crystalline materials, it is often difficult to prepare solid-state films with large-scale perfect domains without structural defects. Applications in optoelectronic and magnetic materials are therefore limited by the ease with which single crystals of a given material can be grown.

Liquid-crystalline materials have self-assembly characteristics for forming various phases and provide additional features such as an ability to respond to applied external fields.⁸ Incorporation of the liquid-crystalline properties into layered materials is expected to bring about the emergence of more functionalized metal-containing thin films.⁹ Metallomesogens, which are metal-containing compounds, have been regarded as a new class of thermotropic liquid crystals.⁹ They have produced new development in the chemistry of liquid-crystalline materials. Inclusion of a metal atom in a molecule results not only in the formation and stabilization of the liquid-crystalline phases but also in the enhancement of properties such as electronic po-

larizability, hyperpolarizability, dichroism, and paramagnetism.^{9,10} The metallomesogens reported so far have a variety of structures but contain some common structural features. In most of the metallomesogens, robust aromatic ligands possessing heteroatoms are attached to the metal atoms through a coordinate bond. The manner of arrangement of the metal atoms in the liquid-crystalline phase depends on the overall molecular geometry of the complex. On the other hand, only few liquid-crystalline coordination compounds with flexible organic ligands have been reported as metallomesogens; primary metal thiolates, $[MSR]$ ($M = Ag, Cu$; $R = n$ -alkyl),¹¹ and amino complexes such as $[CuL_4](NO_3)_2$ and $[AgL_2]NO_3$ ($L =$ alkylamine)¹² have been described so far.

With regard to metallomesogens without flexible or rigid organic ligands, there are tetrahalogenometalate salts, which are composed of divalent metal ions surrounded by four halide ligands and cationic amphiphiles. These ionic metallomesogens are classified into two types according to the structure of the amphiphilic components. One consists of complex salts having alkyl-substituted aromatic cations, such as bis(imidazolium) and bis(pyridinium) tetrahalogenometalate salts.¹³ The other type, which contains monoalkylated nonaromatic cations, is the bis(alkylammonium) tetrahalogenometalate salts, $(RNH_3)_2[MX_4]$, described above.^{3,7} Through intensive studies on structural phase transition behavior (i.e., order-disorder solid-solid phase transition behavior) of the $(RNH_3)_2[MX_4]$ family, a few compounds were suggested to show liquid-crystalline phases in the high-temperature region (over 150 °C).^{7a,d,e} Unfortunately, no clear liquid-crystalline behavior was observed because of thermal decomposition during the heating process. Recently, an ionic salt that is molten at room temperature has also received considerable attention as an ionic solvent possessing superacidity, remarkable solubility, and nonvolatility, as well as unique catalytic behavior.¹⁴ In particular, the use of ionic fluids with thermotropic liquid-crystalline character (i.e., anisotropic solvents) can have a profound effect on the course of chemical reactions (or selective reactions) on account of their inherently ordered nature, i.e., the solvents perform a catalytic role. In applications of the liquid-crystalline complex salts to ionic media as well as the layered thin films, it might be indispensable that they show a liquid-crystalline phase in a wide temperature range around room temperature.

More recently, we reported the thermotropic liquid-crystalline behavior of tetraalkylonium salts,

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$[(C_nH_{2n+1})_2(CH_3)_2HetCl]$ ($n = 10, 14, 18$; $Het = N, P$).¹⁵ Through systematic studies of their thermodynamic properties, the onium species were found to possess an advantageous feature as thermotropic liquid crystals despite being structurally simple amphiphiles without rigid cores. These tetraalkylated ionic amphiphiles showed greater thermal stability and a wider liquid-crystalline temperature range (e.g., 38–155 °C on heating for didecyldimethylphosphonium chloride). In the liquid-crystalline phase, they formed a self-organization with smectic layer structures that is built up from alternating layers of ions and alkyl segments. The ionic layers sandwiched between two alkyl layers can be regarded as functional sites possessing a two-dimensional nature, which are composed of pairs of positive and negative ions as an electric dipole.^{15c,16} Through incorporation of divalent metal ions into the ionic layers, therefore, it will be expected that the tetraalkylated ionic amphiphiles exhibit superior thermotropic liquid-crystalline behavior and form a layered self-assembly consisting of two-dimensional layers of metal ions. Here, we present the thermotropic liquid-crystalline behavior and phase structure of metal complex salts consisting of divalent metal ions with four chloride ligands and the tetraalkylammonium species as a counterion, $[(C_{18}H_{37})(CH_3)_3N]_2[MCl_4]$ and $[(C_{18}H_{37})_2(CH_3)_2N]_2[MCl_4]$ ($M = Co, Ni, Cu, Zn, Cd$), as a novel class of ionic metallomesogens without organic ligands.

Experimental Section

Materials and Methods. The chemical structures of the ionic metallomesogens with tetrachlorometalate ions, **M-1** and **M-2** ($M = Co, Ni, Cu, Zn, Cd$), and the corresponding parent ammonium chlorides without metal ions, **Cl-1** and **Cl-2**, used in this study are shown in Figure 1. The **M-1** and **M-2** complexes are composed of one tetrachlorometalate ion and two amphiphilic components. Octadecyltrimethyl- and dimethyldioctadecylammonium chlorides (**Cl-1** and **Cl-2**) are commercial products (Tokyo Kasei). The anhydrous metal(II) chlorides (Kanto Chemicals) were used without further purification. The **M-1** and **M-2** compounds were prepared from **Cl-1** and **Cl-2**, respectively, with the metal sources in one step.

In a typical preparation, octadecyltrimethylammonium chloride (1.04 g, 3.0 mmol) or dimethyldioctadecylammonium chloride (1.76 g, 3.0 mmol) was dissolved in 20 mL of anhydrous acetonitrile at room temperature. This solution was added dropwise to 100 mL of a stirred anhydrous acetonitrile solution containing 0.5 equiv of the appropriate anhydrous metal(II) chloride ($CoCl_2, NiCl_2, CuCl_2, ZnCl_2, \text{ or } CdCl_2$) at 60 °C, and then the reaction mixture was left with stirring at the same temperature for 3 h. The reaction mixture was allowed to stand overnight in a refrigerator. The precipitated crystalline solid was collected by filtration, washed with anhydrous acetonitrile, and dried under vacuum. The products were purified by recrystallization from anhydrous acetonitrile, and the purification was repeated at least three times.

The tetrachlorometalate salts prepared were characterized by ¹H NMR spectroscopy (Bruker AC200, 200 MHz) and fast atom bombardment mass spectrometry (FABMS; JEOL JMS-AX 505W) in which glycerol was used as an FAB matrix and the positive FAB ionization method (PI) was used at an accelerating voltage of 10 kV with Xe atom as the primary ion source. The purities were examined by elemental analysis

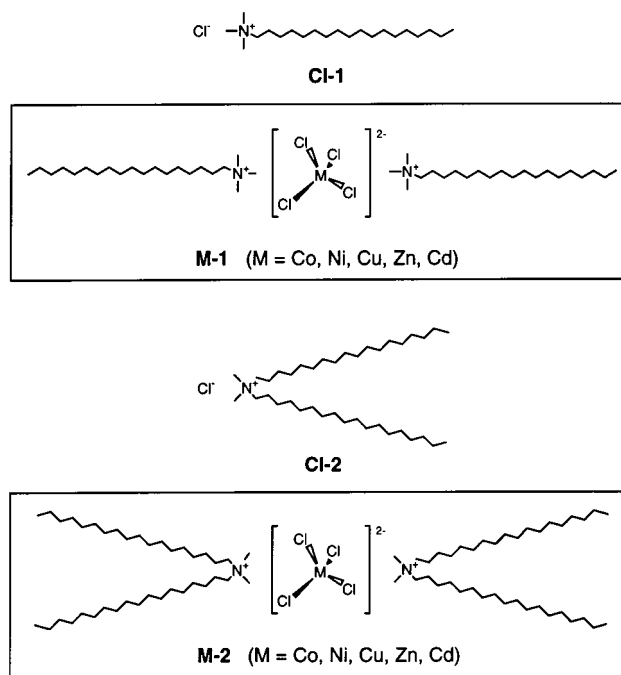


Figure 1. Chemical structures of the ionic metallomesogens (**M-1** and **M-2**) and the corresponding parent compounds (**Cl-1** and **Cl-2**) used in this study.

for C, H, N, and Cl. With regard to measurement of the metal content, each compound (~15 mg) was dissolved in acetone (2 mL). Subsequently, the stock solutions were diluted with distilled water so as to give a concentration of ~10 $\mu\text{g mL}^{-1}$ as a metal content, and then the resulting homogeneous solutions were subjected to inductively coupled plasma (ICP) analysis. For all of the compounds, the found values agreed with the calculated values within the experimental error. The microanalytical data obtained are listed in Table 1.

Evaluation of Thermodynamic Properties. The thermotropic liquid-crystalline behavior of **M-1**, **M-2**, **Cl-1**, and **Cl-2** was evaluated by differential scanning calorimetry (DSC; Seiko I&E SSC-5200 and DSC220C; heating and cooling rate, 5 °C min^{-1}), polarizing optical microscopy (Olympus model BX50, Mettler FP82HT hot stage and Mettler FP90 central processor), and X-ray diffractometry (MAC Science MXP³, equipped with a thermal controller, model 5301).

The phase transition behavior of the complex salts and the corresponding parent compounds was explored by means of DSC. About 10 mg of the fully dried sample was placed in an aluminum sample pan, which was then sealed. The sample pan was placed in the DSC cell compartment and cooled to about -20 °C. Measurements were carried out at a heating rate of 5 °C min^{-1} up to 180 °C. The phase transition temperature was taken as the peak maximum, and the enthalpy change was determined from the peak area. To determine reproducibility, measurements were done in quadruplicate for the same sample. The reproducibilities of the phase transition temperature and the enthalpy were ± 0.2 °C and $\pm 4\%$, respectively. The entropy change was calculated by assuming that the transition was sufficiently reversible. The thermotropic phase transition behavior on heating and cooling for each sample is summarized in Table 2.

In addition, to determine the thermal decomposition temperature of the complex salts, thermogravimetric (TG) assays were conducted with a Seiko I&E TG/DTA220 instrument coupled with a Seiko I&E SDM/5600 thermal analysis station. Experiments were carried out on about 10-mg samples heated in flowing nitrogen (200 mL min^{-1}) at a heating rate of 10 °C min^{-1} . The decomposition temperature was defined as the temperature at which 10% weight loss was recorded by TG. The values estimated are shown in the last column of Table 2.

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Table 1. Microanalytical Data for the Metal Complex Salts and Crystal Appearances

| compd | found (calcd) ^a (%) | | | | | appearance |
|-------------|--------------------------------|---------------|-------------|---------------|--------------------|-------------------|
| | C | H | N | Cl | metal ^b | |
| Cl-1 | 72.35 (72.47) | 13.22 (13.32) | 4.00 (4.02) | 10.02 (10.19) | | white powder |
| Co-1 | 60.81 (61.08) | 11.36 (11.23) | 3.35 (3.39) | 17.06 (17.17) | 7.11 (7.14) | blue powder |
| Ni-1 | 60.78 (61.09) | 11.12 (11.23) | 3.30 (3.39) | 17.27 (17.17) | 6.98 (7.11) | blue powder |
| Cu-1 | 60.46 (60.74) | 11.15 (11.16) | 3.36 (3.37) | 16.77 (17.07) | 7.96 (7.65) | yellow powder |
| Zn-1 | 60.29 (60.60) | 11.37 (11.14) | 3.34 (3.37) | 17.20 (17.04) | 7.72 (7.86) | white powder |
| Cd-1 | 57.15 (57.36) | 10.81 (10.54) | 3.24 (3.19) | 15.87 (16.13) | 12.32 (12.78) | white powder |
| Cl-2 | 77.60 (77.82) | 13.59 (13.75) | 2.26 (2.39) | 6.39 (6.04) | | white powder |
| Co-2 | 69.71 (70.06) | 12.16 (12.38) | 2.14 (2.15) | 10.45 (10.88) | 4.35 (4.52) | blue powder |
| Ni-2 | 69.72 (70.08) | 12.41 (12.38) | 2.04 (2.15) | 10.54 (10.89) | 4.32 (4.51) | blue-green powder |
| Cu-2 | 69.31 (69.82) | 12.12 (12.33) | 2.14 (2.14) | 10.97 (10.85) | 4.95 (4.86) | yellow powder |
| Zn-2 | 69.71 (69.72) | 12.29 (12.32) | 2.14 (2.14) | 10.51 (10.83) | 4.78 (4.99) | white powder |
| Cd-2 | 67.02 (67.30) | 11.98 (11.89) | 2.02 (2.07) | 10.15 (10.46) | 8.04 (8.29) | white powder |

^a Determined by elemental analysis. ^b Estimated by inductively coupled plasma analysis.

Table 2. Thermodynamic Characterization for Phase Transition of the Tetrachlorometalate Salts^a

| compd | heating | | | | | | cooling | | | | | | <i>T</i> _{dec} ^d (°C) |
|-------------|---------------------------------|--|---|---------------------------------|--|---|---------------------------------|--|---|---------------------------------|--|---|---|
| | K → S _A ^b | | | S _A → I ^c | | | K ← S _A ^b | | | S _A ← I ^c | | | |
| | <i>T</i> _{KS} (°C) | Δ <i>H</i> _{KS} (kJ mol ⁻¹) | Δ <i>S</i> _{KS} (J K ⁻¹ mol ⁻¹) | <i>T</i> _{SI} (°C) | Δ <i>H</i> _{SI} (kJ mol ⁻¹) | Δ <i>S</i> _{SI} (J K ⁻¹ mol ⁻¹) | <i>T</i> _{KS} (°C) | Δ <i>H</i> _{KS} (kJ mol ⁻¹) | Δ <i>S</i> _{KS} (J K ⁻¹ mol ⁻¹) | <i>T</i> _{SI} (°C) | Δ <i>H</i> _{SI} (kJ mol ⁻¹) | Δ <i>S</i> _{SI} (J K ⁻¹ mol ⁻¹) | |
| Cl-1 | 101 ^e | 52 ^e | 140 ^e | | | | 92 ^e | 53 ^e | 145 ^e | | | | 233 |
| Co-1 | 59 | 48 | 144 | 153 | 10 | 24 | 49 | 47 | 146 | 143 | 9.4 | 23 | 274 |
| Ni-1 | 57 | 38 | 115 | 151 | 9.3 | 22 | 48 | 37 | 115 | 141 | 9.1 | 22 | 264 |
| Cu-1 | 74 | 92 | 266 | 113 | 6.5 | 17 | 42 | 49 | 156 | 92 | 2.9 | 7.9 | 228 |
| Zn-1 | 59 | 43 | 130 | 151 | 7.4 | 17 | 48 | 40 | 125 | 138 | 7.6 | 18 | 276 |
| Cd-1 | 69 | 87 | 255 | (138 | 2.2 | 5.4) ^f | 44 | 50 | 158 | (120 | 2.4 | 6.1) ^f | 278 |
| | | | | (157 | 3.6 | 8.4) ^f | | | | (153 | 3.6 | 8.5) ^f | |
| | | | | 168 | 7.6 | 17 | | | | 164 | 7.2 | 16 | |
| Cl-2 | 87 | 21 | 59 | 127 | 1.2 | 3.1 | 60 | 17 | 51 | 100 | 1.1 | 2.9 | 211 |
| Co-2 | 45 | 29 | 91 | (131 | 1.7 | 4.2) ^f | 39 | 21 | 133 | (127 | 0.92 | 2.3) ^f | 270 |
| | | | | 155 | 2.6 | 6.1 | | | | 152 | 3.1 | 7.3 | |
| Ni-2 | 44 | 35 | 111 | 145 | 1.3 | 3.1 | 38 | 27 | 87 | 138 | 1.3 | 3.2 | 279 |
| Cu-2 | 36 | 56 | 181 | 134 | 2.9 | 7.1 | 28 | 65 | 216 | 114 | 2.4 | 6.2 | 240 |
| Zn-2 | 50 | 22 | 69 | (130 | 2.8 | 6.8) ^f | 42 | 19 | 60 | (125 | 2.5 | 6.3) ^f | 276 |
| | | | | 145 | 2.4 | 5.6 | | | | 142 | 2.8 | 6.7 | |
| Cd-2 | 49 | 61 | 188 | (137 | 3.4 | 8.3) ^f | 33 | 33 | 108 | (138 | 2.1 | 5.1) ^f | 268 |
| | | | | 163 | 2.4 | 5.6 | | | | 161 | 3.1 | 7.1 | |

^a *T*_{KS} and *T*_{SI}, phase transition temperature; Δ*H*_{KS} and Δ*H*_{SI}, enthalpy change; Δ*S*_{KS} and Δ*S*_{SI}, entropy change. ^b Crystalline- (K) to smectic A (S_A) phase transition. ^c Smectic A- (S_A) to isotropic (I) phase transition. ^d Decomposition temperature at which 10% weight loss occurred, recorded by TG at a heating rate of 10 °C min⁻¹ in N₂. ^e Crystalline- (K) to isotropic (I) phase transition. ^f Polymorphic transition observed in the liquid-crystalline temperature range (S_A-S_A phase transition).

Measurements for Molecular Alignment and Coordination Geometry of the Complex Ions. The X-ray measurements for molecular alignment of the complex salts were done using Cu K_{α1} radiation from a 1.6-kW anode X-ray generator in the liquid-crystalline temperature range. The structural parameters for the liquid-crystalline phases of the samples are listed in Table 3.

To obtain information on the coordination geometry of the tetrachlorometalates in the liquid-crystalline phase, electronic and vibrational spectra of the colored compounds containing Co, Ni, and Cu atoms were measured on a Jasco V-550 UV/vis spectrophotometer and a Jasco NRS-2100 laser Raman spectrophotometer, respectively. In the Raman experiments, an Ar⁺ laser (514.5 nm) was used as the light source, and the spectra were measured at various temperatures at which the samples show a liquid-crystalline phase.

Results and Discussion

Thermodynamic Properties of the Metal Complex Salts. Introduction of divalent metal ions into the common amphiphiles led to enhancement of the thermal properties, as seen in Table 2. In a series of **M-1** with single-long-chain amphiphilic components, all of the compounds showed liquid-crystalline behavior irrespective of the metal atoms. Although **Cl-1** as the corresponding parent compound displayed no liquid-crystalline properties, **M-1** exhibited the smectic A (S_A) phase

Table 3. X-ray Diffraction Data for the Metal Complex Salts

| compd | <i>d</i> ₁ (Å) ^a | <i>d</i> ₂ (Å) ^a | <i>d</i> ₃ (Å) ^a | <i>T</i> (°C) ^b |
|-------------|--|--|--|----------------------------|
| Cl-1 | | | | |
| Co-1 | 33.0 | 17.1 | | 100 |
| Ni-1 | 35.3 | 18.0 | 11.7 | 100 |
| Cu-1 | 33.4 | 16.3 | | 100 |
| Zn-1 | 38.1 | 19.2 | | 100 |
| Cd-1 | 34.2 | 17.7 | 12.2 | 100 |
| | (33.4 | 16.9 | 11.3 | 150) ^c |
| | (32.1 | 16.3 | | 162) ^c |
| Cl-2 | 33.4 | 16.2 | 11.4 | 100 |
| Co-2 | 31.3 | 16.1 | 10.9 | 100 |
| | (28.9 | 15.0 | 10.3 | 140) ^c |
| Ni-2 | 32.5 | 16.5 | 11.2 | 100 |
| Cu-2 | 31.5 | 16.4 | 11.1 | 100 |
| Zn-2 | 32.5 | 16.8 | 11.3 | 90 |
| | (29.8 | 15.7 | 10.6 | 140) ^c |
| Cd-2 | 32.2 | 16.4 | 11.0 | 100 |
| | (30.2 | 15.5 | 10.3 | 150) ^c |

^a *d*₁, *d*₂, and *d*₃ correspond to smectic layer spacings in a liquid-crystalline phase, which were calculated from first-, second-, and third-order diffraction peaks, respectively. ^b Temperature at which the X-ray measurements were performed. ^c Change in the layer spacing due to the S_A-S_A phase transition.

in a wide temperature range (about 100 °C), except for the copper complex **Cu-1**. In addition, the decomposition temperature of each of the metal complexes was higher than that of the parent compound, except for **Cu-1**.

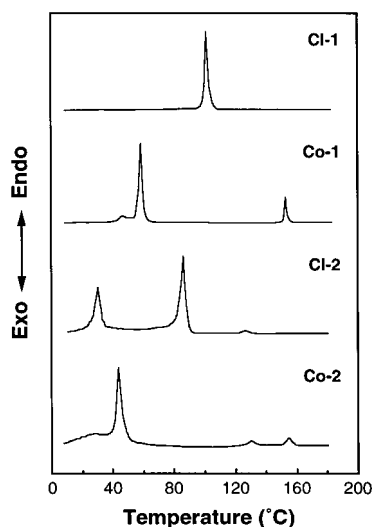


Figure 2. DSC thermograms on second heating scan for the complex salts **Co-1** and **Co-2** as well as the corresponding parent compounds **CI-1** and **CI-2**.

Typical DSC thermograms observed for **CI-1** and **Co-1** in the second heating scan are shown in Figure 2. For all of the **M-1** complexes, we observed clearly the endothermic events that correspond to the crystalline-(K) to- S_A phase transition and the S_A -to-isotropic (I) phase transition. Both the K-to- S_A and S_A -to-I phase transitions occurred with no change in the baseline, i.e., no change in the heat capacity. As shown in Table 2, entropy change (ΔS_{SI}) at the S_A -I phase transition for **M-1** in the heating run was in a range from 17 to 24 J K⁻¹ mol⁻¹. These results clearly indicate that, in the simple salts without rigid components, the divalent metal ions play an important role in the formation of the liquid-crystalline phases and the enhancement of the thermal stability.

A similar trend was observed for a series of the complex salts having double-long-chain cations. Although the parent salt **CI-2** showed the S_A phase in a temperature range from 87 to 127 °C on heating, the phase transition behavior was quite indistinct. As depicted in Figure 2, the DSC signal corresponding to the S_A -I phase transition was quite weak, and a K-K transition (or solid-solid transition) was observed in the low-temperature region, which is basically ascribed to a dynamic order-disorder transition of the alkyl chains. On the other hand, the **M-2** complexes exhibited clear phase transition behavior and a stable liquid-crystalline phase in an expanded temperature range in comparison with the parent compound (see Table 2 and Figure 2). Such enhancement of the liquid-crystalline properties is obvious also from the fact that the values of ΔS_{SI} of the **M-2** compounds were higher than that of **CI-2**.

Molecular Alignment Behavior in the Liquid-Crystalline Phase. To explore the molecular alignment behavior of the complex salts, observation of the optical textures was performed first by means of polarizing optical microscopy. During the first heating scan, **M-1** and **M-2** showed an oily streak texture exhibiting smectic-like character in the liquid-crystalline temperature range. On the other hand, no optical texture was observed even at the liquid-crystalline temperature when the sample was heated to a temperature higher than T_{SI} and then gradually cooled to a temperature

below T_{SI} . By application of a shearing stress to the samples, however, fan-shaped texture consistent with an S_A phase appeared, resulting from enhancement of conformational freedom of the long alkyl chains. These results demonstrate that the complex salts show smectic layers in which homeotropic structures are formed spontaneously, i.e., the molecules are aligned perpendicular to the glass substrates.

The liquid-crystalline phase structure of the ionic metallomesogens was evaluated by X-ray powder diffraction in more detail. The X-ray diffraction data obtained for both **M-1** and **M-2** are summarized in Table 3. For instance, in the cobalt complexes, the first-order diffraction angles indicate that the **Co-1** and **Co-2** molecules pack into layers with d spacings of 33.0 and 31.3 Å, respectively. Although the calculated layer thickness in each compound is slightly smaller than the molecular length in the most extended conformation, it is at least true that the molecular long axis is nearly perpendicular to the layer plane. Furthermore, the diffraction patterns gave one or two higher-order Bragg reflections (see Table 3). This result suggests that the liquid-crystalline organization formed by the complex salts is composed of a highly ordered multilayer structure that is built up from alternating layers of ions and alkyl segments. In other words, the ionic layers could be regarded as two-dimensional sheets of metal complexes sandwiched between two ammonium layers. A similar molecular arrangement with the S_A phase was also observed for the other complex salts having different metal atoms (see Table 3).

Ionic amphiphilic liquid crystals with long hydrocarbon chains are known to exhibit a thermotropic smectic character, resulting from chain-melting of hydrophobic moieties.^{13,17} In the liquid-crystalline phases, even after the alkyl chains have melted, the ionic bonding between a polar head and counteranions remains unchanged, and free molecular motion of the amphiphiles is prevented by the rigidity of the ionic layers because of the ionic interaction between the polar heads. The ionic aggregation of the amphiphiles contributes to the formation of the smectic layer structure. The interlayer bonding is achieved not only by van der Waals forces between the terminal methyl or nearby alkyl groups of adjacent layers, but also by long-range Coulomb forces.^{7c} It is assumed, therefore, that the advantageous thermodynamic properties of the **M-1** and **M-2** complex salts arise from an enhancement of the interlayer as well as intralayer Coulomb interaction through the introduction of metal ions into the **CI-1** and **CI-2** parent compounds. Moreover, the intrinsic liquid-crystalline property of **M-1** and **M-2** seems to be attributed to the structure of the polar groups of the ammonium components as a counterion. In the case of the $(RNH_3)_2[MX_4]$ compounds with mono-alkylated ammonium ions as described above,

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the ammonium heads are attached from both sides to the $[\text{MCl}_4]^{2-}$ sheet through hydrogen bonding to the halide atoms.^{3,7c,f,g} The presence of such hydrogen bonds would enhance crystallization and prevent the appearance of liquid-crystalline or isotropic phases with fluidity. Because **M-1** and **M-2** contain tetraalkylammonium ions instead of RNH_3 groups, they are unable to form hydrogen bonding between the ammonium layer and the tetrachlorometalate layer. Thus, the structural character of the tetra-substituted ammonium ions might enable formation of the fluid phase.

Additionally, to explore the coordination geometry of the tetrachlorometalate ions in the liquid-crystalline phase, we measured the UV/vis absorption spectra of the colored **M-1** and **M-2** complexes. In all of the compounds, the d-d band (i.e., the ligand-field absorption band) was observed in the visible region. Through the assignment of the absorption bands, it was found that the metal centers in **M-1** and **M-2** unsurprisingly have tetrahedral geometries even in the liquid-crystalline phase, which is consistent with the geometry of a range of tetra-substituted onium salts containing $[\text{MCl}_4]^{2-}$ species in the crystalline phase. The existence of the $[\text{MCl}_4]^{2-}$ tetrahedron in the liquid-crystalline phase was confirmed also by Raman spectroscopy.

A Distinct S_A - S_A Phase Transition in the Ionic Metallomesogens. Through calorimetric investigations, some of the compounds in the series **M-1** and **M-2** were found to exhibit enantiotropic polymorphism in the liquid-crystalline phases. As seen in Figure 2 and Table 2, **Cd-1**, **Co-2**, **Zn-2**, and **Cd-2** each showed a transition between two liquid-crystalline phases. The X-ray diffraction and optical polarizing microscopic studies demonstrated that there is no evidence for nematic or higher-order smectic phases. The most probable explanation for the observed unique transition is an S_A -to- S_A phase transition. In the conventional liquid crystals, it is known that several compounds show different S_A phases through an S_A - S_A phase transition, which are classified into five types according to the molecular or dipolar array in the S_A phase.¹⁸ These compounds have polar groups (such as cyano and nitro groups) as terminal functions in the rodlike molecules with elongated rigid aromatic cores, and such structural features lead to large dipole moments along the long axis of the molecules. In the S_A - S_A transition behavior, therefore, an intermolecular or interlayer dipole-dipole interaction seems to play a very important role. On the other hand, **M-1** and **M-2** include neither polar groups attached to the rigid aromatic cores nor dipole moments along the molecular long axis. Thus, the specific phase transition observed in the present study differs essentially from the S_A - S_A transition discovered in the existing liquid crystals.

We inferred that the polymorphic transition of **M-1** and **M-2** is ascribed to a change in the layer thickness

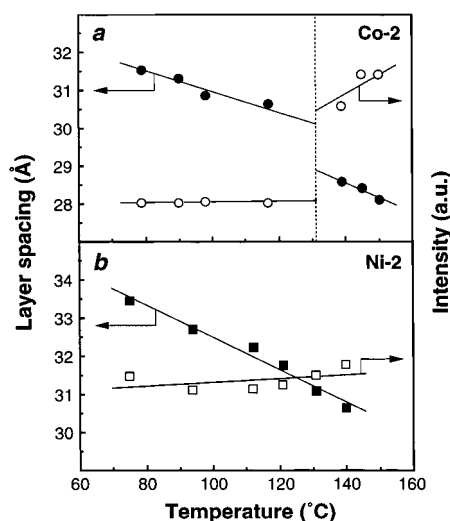


Figure 3. Changes in the layer thickness and the degree of orientational order in the smectic A phase: (a) **Co-2** showing a polymorphism in the S_A phase, (b) **Ni-2** showing no polymorphic transition, (● and ■) smectic layer spacing, (○ and □) intensity of the lowest diffracted X-ray signals.

with temperature, which is due to changes in conformation change (or intralayer packing manner) in the melted alkyl segments. This prediction was verified first by the X-ray diffraction analysis. Figure 3 shows the temperature dependence of the layer spacing of **Co-2** and **Ni-2** in the S_A phase. The layer thickness of each sample was found to decrease with temperature, irrespective of the metal atom. On the other hand, in the case of the nonmesogenic $(\text{RNH}_3)_2[\text{MX}_4]$ analogues, it has been reported that the layer thickness increases with temperature as a general tendency.^{7b,g} Thus, the observed phenomenon could be specific for the liquid-crystalline tetrahalogenometalate salts. It is worth mentioning here that the layer spacing of **Co-2** changed discontinuously at around 130 °C, which corresponds to the S_A - S_A transition temperature (closed symbols in Figure 3a), and the intensities of the X-ray diffraction signals in the high-temperature liquid-crystalline phase were much higher than those in the low-temperature region (open symbols in Figure 3a). A similar tendency was also observed on cooling. In contrast, such discontinuous changes in the layer thickness and in the diffraction peak intensity were not observed in **Ni-2**, which exhibited no polymorphism (Figure 3b). The compounds without an S_A polymorphism such as **Ni-2** would show only the high-temperature type of S_A phase because the values of ΔH_{S1} and ΔS_{S1} are approximately the same order for each series, irrespective of the metal ions. These results suggest the validity of our hypothesis concerning the S_A - S_A transition. However, it is not well understood at the present stage of research why the degree of orientational order is enhanced in the high-temperature liquid-crystalline phase. To obtain information on the internal order within a layer in the low- and high-temperature S_A phases, we also estimated the average lateral area occupied by a single molecule from the broad X-ray diffraction peaks in the high-angle region. The values of the occupied area or the lateral molecular spacing, however, were unchanged at the

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S_A – S_A transition. Unfortunately, the observed S_A polymorphism cannot be interpreted in terms of the area occupied by a molecule.

Conclusions

The metal complex salts, which are structurally simple compounds without organic ligands consisting of tetrachlorometalate ions and tetraalkylammonium ions, were found to exhibit advantageous features as thermotropic liquid crystals (metallomesogens) and a new type of polymorphism in the liquid-crystalline phase. These phase structures were characterized as

smectic A, in which a layered structure with a two-dimensional array of tetrahedral metal ions was formed spontaneously. The structural and electronic features of the metal-containing layered structures were also described to be variable through an S_A – S_A phase transition. We expect that the liquid-crystalline complex salts prepared in this study will be even more favorable for applications to functionalized materials such as metal-containing layered thin films and anisotropic ionic solvents.

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