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Mesogenic Behavior of Silver Thiolates with Layered Structure in the Solid State: Covalent "Soaps"

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Abstract: The family of primary silver thiolate compounds $AgSC_nH_{2n+1}$ (n = 4, 6, 8, 10, 12, 16, and 18), which in the solid state consist of $^2_\infty$[AgSR] layers with the R substituents extending perpendicular to both sides of a central slab of Ag and S atoms, behave as thermotropic liquid crystals. On heating they display successively lamellar (smectic A), cubic, and micellar mesophases; the range of appearance of the two former phases decreases with increasing length of R, so that for $n \geq 12$ only the micellar phase is observed on melting. X-ray diffraction studies on the lamellar phase for $n = 6$ reveal a packing rather similar to that found in the solid. For $n = 18$, X-ray diffraction shows that the micellar phase is a hexagonal columnar mesophase, which is understood as being the result of a rearrangement of the solid-state structure to form $(AgSR)_8$ cyclic structures behaving as micelles.

Introduction

Metallomesogens (metal-containing compounds displaying liquid crystalline behavior)[1] are a rapidly growing new class of mesogens (materials giving rise to liquid crystallinity) where the study of the relationships between structure and mesogenic behavior, which is reasonably developed for organic mesogens, is in its infancy.

Most metallomesogens reported so far are based on very anisotropic rod- or disk-shaped discrete molecules consisting of a rigid core bearing one or more flexible hydrocarbon chains (Figure 1) and give rise to nematic, smectic, or discotic mesophases.

The role of the metal atom varies from a simple link between promesogenic moieties (Figure 1a,b)[2] to being the organizer of a rigid core (Figure 1d).[3] Even in cases when the metal atom acts apparently as a simple end-substituent in a promesogenic organic moiety (Figure 1c), the appearance of mesomorphism from nonmesogenic ligands shows the important effect of the metal atom in increasing intermolecular attractions.[4] There are a few cases (Figure 2) where the presence of a metal atom leads to molecular shapes rather different from those usually found in organic mesogens, such as the ferrocene derivatives,[5] the open-book (or roof) shaped palladium dimers,[6] or polymers where the metal is the link for polymerization.[7]

The bilayer organization common in ionic amphiphilic or polar mesogens, such as alkali-metal soap in its "neat-soap" lamellar mesophase,[8] is very slightly represented in metallomesogens: only $(n\text{-}C_nH_{2n+1}NH_3)_2[MX_4]$ (X = halogen) mesogenic species, having a cationic surfactant structure, have been described.[9] The type of organization existing in the few other thermotropic ionic metallomesogens described so far—$[AgL_2]X$ (L = 4-substituted pyridine)[10] and $[CuL_4](NO_3)_2$ (L = alkylamine)[11]—has not been studied, but the fact that both have the metal ion in the center of a rigid core rather than as a polar end suggests that their mesogenic structures might show marked differences with respect to a typical bilayer organization.

For this reason a recent paper by Dance et al.[12] revealing the layered structure of crystalline compounds AgSR attracted our attention. This structure consists basically of a central plane of silver atoms—in a quasihexagonal arrangement—connected by bridging μ^3-SR groups extending perpendicular to the central slab on both sides. If these compounds were able to resist heating without severe decomposition, melting of the chains preserving the bilayer structure might produce lamellar (or smectic A) mesophases similar to those found for ionic amphiphiles, but based on a covalent rather than an ionic interaction. One should take into consideration that, since thermal motion increases the actual bulkiness of the R groups, heating might also produce a structural change from $^2_\infty$[AgSR] to the cyclic molecules $[AgSR]_x$ (x = 3, 4, 8, 12) found with bulky R groups.[13]

Having this in mind, we set out to prepare a series of primary silver thiolates, $AgSC_nH_{2n+1}$, and study their thermal behavior. The recognition of their mesogenic character by hot stage po-

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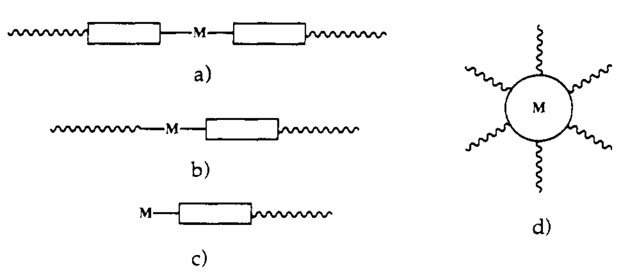

Figure 1. Common molecular shapes in metallomesogens. M stands for the metal atom plus non-promesogenic ligands (e.g., M = *trans*-$PtCl_2$, *cis*-$RhCl(CO)_2$, etc.).

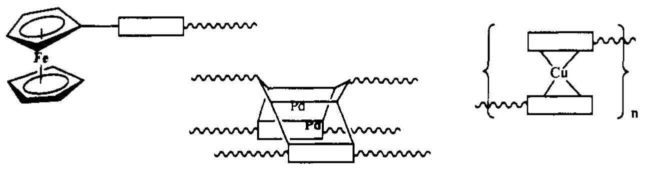

Figure 2. Unusual molecular shapes giving rise to metallomesogens.

larizing optical microscopy, differential scanning calorimetry, and X-ray diffraction studies of the mesophases of two derivatives is reported here.

Experimental Section

Materials and Techniques. All the thiols used were commercial (Aldrich) grade and were not submitted to further purification. Their catalogue purities were all over 97% purity except for $HSC_{16}H_{33}$ whose catalogue purity was 92%. No commercial source of $HSC_{14}H_{29}$ was found. Combustion analyses were made with a Perkin-Elmer 240B microanalyzer. Microscopic studies were carried out in a Leitz microscope provided with a hot stage and polarizers at a heating rate of ca. 5 °C min^{-1}. For differential scanning calorimetry a Perkin-Elmer DSC7 instrument was used, which was calibrated with water and indium; the scanning rate was 5 °C min^{-1}, the samples were sealed in aluminum capsules in the air, and the holder atmosphere was dry nitrogen.

X-ray diffraction experiments were performed with a Guinier camera with Cu Kα radiation and a cylindrical film of 114.6-nm diameter (powder) or with a point focussing beam with Cu Kα_1 and a flat film (mesophases). The samples were held in Lindeman glass tubes, rotating around their axes in the powder pattern experiments; in the point focussing camera the tubes were situated in the gap of a magnet with a field strength of 0.3–1.7 T.

Preparation of Compounds. All $AgSC_nH_{2n+1}$ were prepared according to the following procedure: To a solution (or a suspension for $n = 16$, 18) of the corresponding thiol (2 mmol) and triethylamine (2 mmol) in acetonitrile (5 mL) at room temperature (18 °C) with stirring at 450 rpm was added a solution of $AgNO_3$ in the same solvent (2 mmol of $AgNO_3$ in 10 mL of solution) at a constant rate of addition of 1 mL min^{-1}. Once the addition was finished, the mixture was stirred for 10 min (60 min for $n = 16$, 18) and the resulting precipitate was filtered, washed with acetonitrile (3 × 2 mL), and vacuum dried. Yields were virtually quantitative. The synthesis and handling of the compounds were precautionarily carried out whenever possible in the dark, but the isolated compounds proved to be rather light stable. All compounds gave satisfactory C, H analysis. *Note*: The synthesis of the compounds with $n = 4$, 6, and 8 has been cursorily reported by Dance et al.[12] Although the compounds analyze satisfactorily for AgSR regardless of usually minor synthetic details, we note that the mesogenic behavior (and also the color of the compound, ranging from almost white to yellow) is rather sensitive to the synthetic conditions used, mainly to the rate of addition of $AgNO_3$.

Results

All $AgSC_nH_{2n+1}$ compounds studied display mesogenic behavior above their melting points, except the ethyl derivative which decomposes at 170 °C without melting. Different preparations of the same complexes varying the concentrations of the reactants and the rates of mixing revealed that these conditions have a noticeable influence (particularly for $n \leq 10$) on the temperatures at which the different mesophases appear; these temperatures also change with the rate of heating in the thermal experiments.

Melting produces some change in color from pale yellow to reddish yellow, particularly in the borders of the drop. For compounds prepared and studied under the strict conditions described in the Experimental Section, the thermal behavior (by microscopy) of $AgSC_nH_{2n+1}$ (n = 4, 6, 8, 10, 12, 16, and 18) is represented in Figure 3, and thermal parameters (by DSC) are collected in Table I.

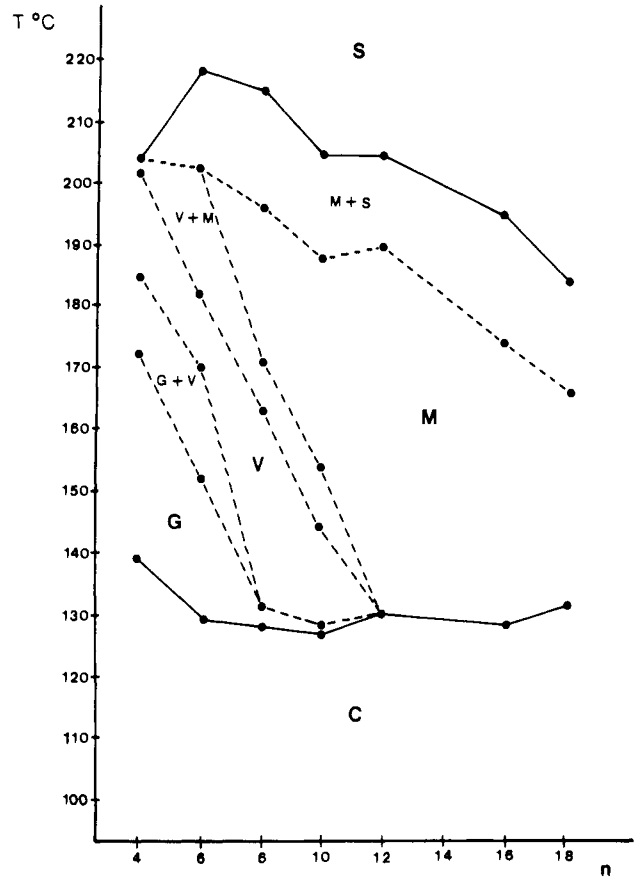

Figure 3. Plot of transition temperatures for $AgSC_nH_{2n+1}$ as a function of the thiolate chain length: (C) crystal, (G) lamellar (smectic A), (V) cubic, (M) micellar, (S) amorphous.

Table I. Thermal Parameters (DSC) for the Different Transitions

n =	transition	T,[a] °C	ΔH, kJ mol^{-1}	ΔS, kJ mol^{-1} K^{-1}
2	decomposes			
4	C–G	139.6	9.5	2.3×10^{-2}
	G–V	166.7	1.7	3.9×10^{-3}
	V–M	177.7	−0.9	-2.0×10^{-3}
	M–S	204.0[b,c]		
6	C–G	128.9	16.5	4.1×10^{-2}
	G–V	152.2	0.3	0.7×10^{-3}
	V–M	167.7	−2.7	-6.1×10^{-3}
	M–S	210.0[b,c]		
8	C–G	128.3	24.7	6.2×10^{-2}
	G–V	133.1	0.5	1.2×10^{-3}
	V–M	172.3	−3.4	-7.6×10^{-3}
	M–S	207.0[b]		
10	C–G	129.4	32.4	8.1×10^{-2}
	G–V	130.0[b]		
	V–M	166.2	−2.7	-6.2×10^{-3}
	M–S	197.0[b]		
12	C–M	131.3	43.8	10.8×10^{-2}
	M–S	178.8	−1.9	-4.2×10^{-3}
16	C–M	128.6	52.7	13.1×10^{-2}
	M–S	173.5	−2.4	-5.4×10^{-3}
18	C–M	131.3	59.4	14.7×10^{-2}
	M–S	175.0[b]		

[a] Measured at the maximum (or minimum) of the peak. [b] Optical data, not detected by DSC. [c] Decomposes.

It is apparent from Figure 3 that a dramatic change in mesogenic behavior occurs from the beginning to the end of the series. In order to discount that this change was related to a change of structure in the solid, the crystalline phase of the derivative with

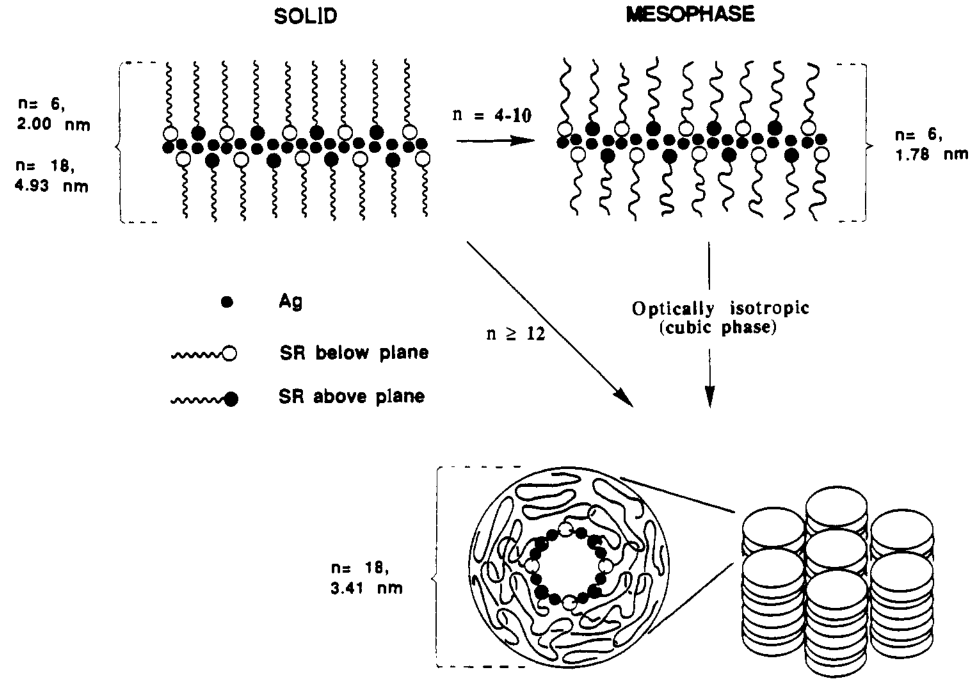

Figure 4. Schematic representation of the structure of silver thiolates in the solid, the lamellar (smectic A), and the micellar mesophases. Only one micelle viewed in the direction of the columnar packing is shown; the micellar mesophase consists of a hexagonal columnar packing of these micelles which can be assimilated to disks 0.5 nm thick.

the longest chain ($n = 18$) was studied by X-ray diffraction; its structure is similar to that found by Dance et al. for the *n*-butyl, *n*-hexyl, and *n*-octyl derivatives, $^{2}_{\infty}[AgSC_{18}H_{37}]$ layers with a layer periodicity of 4.93 nm (for 10 orders of reflections observed). Thus it can be assumed that for the series studied the solid-state structure remains basically the same, with the only variation an increase in the total thickness of the layer as a function of the length of the *n*-alkyl chain.

For $n = 4$–10 melting of the $AgSC_nH_{2n+1}$ compounds leads initially in each case to a lamellar mesophase which shows with polarizing microscopy (after rubbing) a typical homeotropic texture with extinction crosses[14] and oily streaks on heating; on cooling from the cubic phase above it (see below), a fan-shaped focal conic texture is observed. This lamellar phase has been studied by X-ray diffraction for $n = 6$. On melting, the large-angle sharp rings observed in the crystalline phase disappear and a very broad diffuse halo is seen in the range of $2\pi/0.5$ to $2\pi/0.4$ nm^{-1} scattering vectors. Two sharp reflections are observed at small angles corresponding to a lamellar phase of 1.78 nm periodicity. The normal of the layer orients parallel to the magnetic field. This phase is similar to the smectic A phases of comb-like polymers and can also be labeled as a thermotropic smectic A phase (S_A).

Above this S_A phase an apparently isotropic phase (uniformly dark between crossed polarizers) is formed, but further heating gives rise to a new mesophase showing fan-shaped textures; on cooling from the isotropic phase above it, bâtonnets and platelets are formed which are characteristic of a micellar mesophase.[14,15] The logical conclusion is that the apparently isotropic phase separating the lamellar (S_A) and the micellar phases is a cubic phase, optically isotropic, and this is supported by preliminary X-ray results.

The lamellar and cubic ranges decrease with increasing length of the aliphatic chain, so that for $n \geq 12$ melting of the $AgSC_nH_{2n+1}$ compounds produces in each case the micellar mesophase (showing simultaneously zones with schlieren and fan-shaped textures); presumably the other two phases should form as transient intermediates, but we have been unable to detect them. The micellar phase for $n = 18$ has been characterized by X-ray diffraction as a hexagonal columnar mesophase. The four first diffraction rings are seen and the lattice constant is 3.41 nm. Assuming that the micelles are $(AgSR)_x$ cyclic structures with the chains in the outer part of the cycle, the data are consistent with a packing of $(AgSR)_8$ rings with an intracolumnar distance of 0.5 nm and a mean chain area at the interface of the methyl end groups of 0.68 nm^2. In the isotropic phase, $AgSC_{18}H_{37}$ shows two small-angle broad diffuse rings which are not closely related to the structure of the mesophase. The first ring corresponds to an intermicellar distance of 3.8 nm, and the second (which is very weak) to a distance of 1.7 nm.

Differential scanning calorimetry results are rather sensitive to the heating rate, and the results in Table I correspond to a heating rate of 5 °C min^{-1}. Prior to melting, the compounds usually undergo a low-enthalpy endothermic crystal-to-crystal transition. In the compounds displaying the three mesophases, the crystal-to-smectic transition appears as a very clear endothermic peak which is followed by a weakly endothermic smectic-to-cubic transition and a weakly exothermic cubic-to-micellar transition. For $n \geq 12$ only an endothermic peak at the melting temperature is observed which might well be overlapping the other two low-enthalpy transitions. The transitions to the isotropic phase occur gradually over 10–20 °C even at slow heating rates, and the low enthalpic change involved sometimes cannot be detected. Also the other transitions occur slowly, giving rise to ranges of coexistence of two mesophases which are reflected in Figure 3 as observed by polarizing microscopy.

Discussion

The results presented above show that silver thiolates $[AgSC_nH_{2n+1}]_x$ display thermotropic behavior giving rise (Figure 4) to lamellar (smectic A), cubic, and micellar phases; large aliphatic chains favor early appearance of the latter.

Lamellar and micellar mesophases for a given compound are commonly found in lyotropic liquid crystals[8,16] and also contribute to the thermal behavior of some amphiphilic and ionic substances such as some phospholipids[17] or the well-known sodium carboxylates (soaps).[18] On the other hand, columnar mesophases are usually induced by covalent molecules which are disk shaped and consequently prone to this kind of stacking.[3,19] In more general

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terms, the organization found in liquid crystals based on covalent molecules is very dependent on the molecular shape (in addition to other factors), whereas dramatic changes in organization such as changing from a bilayer to a micellar organization (which is the case of silver thiolates) have only been observed in systems based on less directional interactions such as ionic or hydrogen bond interactions.

Thus the system discussed here is an unusual case of a covalently based system with "undefined" basic geometry and packing preference, due to the ability of thiolates to change from μ^3- to μ^2-bridging (and silver from trigonal-planar to linear coordination) depending on other circumstances such as steric requirements; this, in a sense, makes the covalent silver–sulfur interaction less directionally defined. Since their overall thermal behavior resembles that of classic soaps, these silver thiolates can be referred to, in what concerns their thermal behavior, as covalent "soaps".

Apparently the bilayer structure observed in the solid for primary silver thiolates is still the most efficient packing of melt chains (melting of chains involves the appearance of gauche conformations moving up and down the chains)[20,9] while these are not very long and the temperature is not very high. In longer chains or at higher temperatures, however, the disorder induced by melting causes the chains to curl, consequently requiring less length and more thickness; under these circumstances the primary chains have spatial requirements more like those of secondary or tertiary chains, and the silver thiolate changes from its bilayer μ^3-bridged structure in the solid to a cyclic μ^2-bridged structure in the mesophase. This curling of the chains is reflected in the large variation observed for $n = 18$ from the layer periodicity in the solid (4.93 nm) to the lattice constant in the micellar mesophase (3.41 nm, diameter of the disk), compared to the small variation observed for $n = 6$ (2.00 nm in the solid, 1.78 nm in the lamellar mesophase). An intermediate cubic phase appears for which we have no structural proposal at this time (the structure of cubic phases is a difficult and controversial subject),[8a,15,16,21] but we take the exothermic character of the cubic-to-micellar transition as an indication that it is in this transition when the μ^3 to μ^2 bond rearrangement occurs.

The bilayer structure found for the lamellar mesophases can be looked at as a slab of silver of roughly one atom thickness having SR groups stacked at both sides of the slab. The geometrical analogy of crystalline AgSR compounds and the crystalline or liquid-crystalline monolayers of thiols that can be formed on clean gold surfaces[22] has been noticed previously, although differences have also been noted.[12] In the mesophase, which offers the possibility of working on single bilayers in appropriate devices, some of the differences between bulk crystals and monolayers might be overcome. In addition, whereas rigid coordination in the solid state gives rise to pin (SR up) or hole (SR down) sites in the center of each Ag_3 triangle of the silver hexagonal slab, in the mesophase the ease of μ^3-SR to μ^2-SR conversion might well provide a mechanism for the thiolate groups to acquire a more isotropic time-averaged distribution by exchanging pin and hole sites; our techniques do not provide information about this interesting possibility.

Finally, the influence of both the synthetic conditions and the thermal history on the mesogenic behavior of these silver thiolates deserves some comment. These phenomena are rather uncommon in metallomesogens, which are at present represented mainly by molecular materials. It is important to realize that the materials dealt with in this paper are polymeric, and minor changes (even below the level of detection by X-ray powder diffraction) in the solid-state structure, affecting the up and down SR distribution or the level of disruption of the ideally infinite layer structure, will be reflected in the subsequent thermal behavior of the material just as tacticity or degree of polymerization affects the behavior of an organic polymer.

Preliminary results show that CuSR systems seem to behave rather similarly, and it is likely that the mesogenic behavior of related systems has gone unnoticed in the past. Further structural studies on these mesophases and the influence of synthetic and thermal histories on the behavior of MSR (M = Ag, Cu) mesogens are in progress.

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Registry No. $AgSC_4H_9$, 70247-07-3; $AgSC_6H_{13}$, 4081-53-2; $AgSC_8H_{17}$, 4081-38-3; $AgSC_{10}H_{21}$, 140203-09-4; $AgSC_{12}H_{25}$, 140203-10-7; $AgSC_{16}H_{33}$, 140203-11-8; $AgSC_{18}H_{37}$, 45239-84-7.

Supplementary Material Available: Tables with C, H analyses, X-ray data (powder) for [$AgSC_{18}H_{37}$], and X-ray data (mesophase) for [$AgSC_6H_{13}$] and [$AgC_{18}H_{37}$] and DSC curves for four representative [AgC_nH_{2n+1}] (n = 6, 8, 16, 18) (5 pages). Ordering information is given on any current masthead page.

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