Ionic Amphiphilic Metallomesogens

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Synthetic and structural studies on the silver derivatives [Ag(**1**)]X (X = CF_3SO_3 (**2**) or PF_6 (**3**) wherein **1** = 1,10-bis[4-(dodecyloxy)benzoyl]-1,10-diaza-4,7,13,16-tetrathiacyclooctadecane) are reported. The complexes were found to display thermotropic and lyotropic mesomorphism. The mesomorphism of **2** and **3**, investigated by optical, calorimetric, and diffractometric techniques, is discussed on the basis of a bilayered organization of the U-shaped cations. Crystal data for **3**: $P1$, $a = 9.278(2)$ Å, $b = 11.527(3)$ Å, $c = 27.588(7)$ Å, $\alpha = 100.66(2)°$, $\beta = 90.20(2)°$, $\gamma = 92.99(2)°$, $V = 2896(1)$ Å^3, $Z = 2$. Final R and $R_w = 0.062$ and 0.059, respectively.

Introduction

Metallomesogens (metal-containing liquid crystals) very likely represents the fastest growing area in liquid-crystals research.[1,2] Albeit most research groups are currently pursuing materials exhibiting specific properties such as ferroelectricity,[3] many efforts are still devoted to the synthesis of metallomesogens which present unconventional molecular structures and/or unusual mesomorphic properties.[4]

Although the amphiphilic alkali and alkaline earth "soaps" were among the first liquid crystals to be recognized,[5] ionic metallomesogens (thermotropic,[6] lyotropic,[7] or amphotropic[8,9]) are a poorly represented class of mesogens and recognition of their liquid crystallinity relies to a large extent upon X-ray scattering observations.[10,11] Extensive X-ray investigations are therefore needed to reveal the type of organization in ionic systems. In particular, single-crystal X-ray studies would give a valuable answer to the problem of the shape of the discrete mesogens and their packing in the solid state,[12] although the latter is not necessarily related to the mesophase structure.[13]

The macrocyclic N,S mixed-donor ligands 1,10-bis[4-(*n*-alkyloxy)benzoyl]-1,10-diaza-4,7,13,16-tetrathiacyclooctadecane (**L**) were designed[14] with the purpose of obtaining a versatile series of molecules with a rodlike molecular shape. As ligands they were supposed to easily afford either square-planar or tetrahedral recognition.[15] The series of mesogenic copper(I) complexes [Cu(**L**)][PF_6] have been thereupon investigated which exhibited a single mesophase with lamellar structure.[11] The X-ray diffraction (XRD) data on powder samples were explained on the basis of a molecular model with a calamitic shape (tetrahedral coordination geometry at the metal with the two aliphatic chains extending in opposite directions). Although our suggestion for the mesophase structure did not fully explain all the XRD features, the proposed model was reasonable and the possibility of formation of asymmetric cations was not considered.

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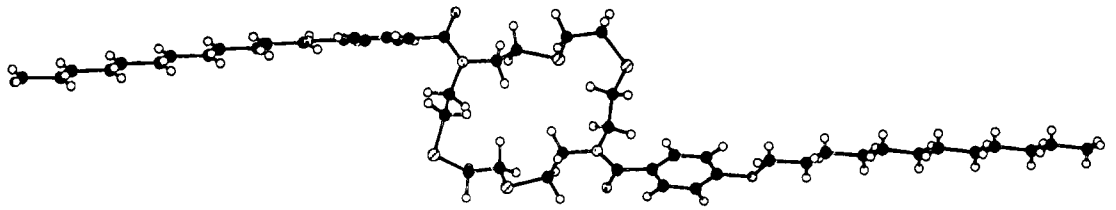

Figure 1. View of ligand **1** with chains in all-anti conformation (drawn using the X-ray data for 1,10-bis(4-chlorobenzoyl)-1,10-diaza-4,7,13,16-tetrathiacyclooctadecane[16]).

Since our attempts to grow single crystals of any of the copper complexes were frustrated, we hoped to get better results with the analogous silver(I) derivatives (isoelectronic and possibly isostructural to Cu(I)). In this light, we concentrated our efforts on the reactivity of different silver salts with the *n*-dodecyloxy homologue (hereafter **1**), a ligand with a good length/breath ratio (Figure 1) and which afforded the copper mesogen with the most clear mesomorphism.[11] We report herein that ionic silver(I) derivatives of **1** have indeed an amphiphilic character which leads to a bilayer organization of the double-chained amphiphiles.

Experimental Section

Materials. All solvents (Aldrich) were reagent grade and were distilled before use. $AgPF_6$ and $AgCF_3SO_3$ were purchased from Aldrich Chemical and used without further purification. The ligand 1,10-bis[4-(*n*-dodecyloxy)benzoyl]-1,-10-diaza-4,7,13,16-tetrathiacyclooctadecane (**1**) was obtained as previously described.[14]

Measurements. Experimental procedures for the characterization of the silver complexes were the same as described before.[11]

X-ray diffraction experiments on powder samples were performed on samples aligned on thin mica plates and quenched to room temperature, using a point focusing monochromatic Cu Kα beam diffracted by a doubly bent pyrolitic graphite monochromator.

Synthesis. The synthesis of the complexes was performed under a dry nitrogen atmosphere trying to minimize exposure of the reaction mixtures to visible light.

[Ag(**1**)][X] (X = CF_3SO_3 (**2**), PF_6 (**3**)). To a stirred solution of **1** (0.1 mmol) in CH_2Cl_2 (4 mL) was added a solution of AgX (0.1 mmol) in CH_3CN (5 mL). The resulting colorless solution was stirred at room temperature for 30 min, whereupon it was filtered through Celite. The solvent was removed under reduced pressure and the solid residue redissolved in the minimum amount of CH_2Cl_2. Addition of *n*-hexane and overnight storage at −20 °C afforded a white solid product. Compound **2**: yield, 79%; Λ_M (1×10^{-4} M in CH_3NO_2) 79.1 Ω^{-1} mol^{-1} cm^2. IR-FT (cm^{-1}, KBr) 2923, 2853, 1626, 1608, 1296, 1224, 1171, 1029, 840, 638. ^{1}H NMR (300 MHz, 298 K, CD_3NO_2): δ 0.86 (t, 3 H), 1.28−1.46 (m, 18 H), 1.78 (m, 2 H), 2.95 (t, 8 H), 2.99 (s, 8 H), 3.75 (t, 8 H), 4.03 (t, 2 H), 7.53 (d, 2 H). ^{13}C{^{1}H} NMR (75.5 MHz, 298 K, CD_3NO_2) δ 13.84, 23.07, 26.48, 29.65, 29.77, 29.83, 30.05, 30.08, 30.10, 32.13, 32.38, 33.03, 49.06, 69.08, 115.16, 129.13, 129.83, 161.51, 174.39. Anal. Calcd for $C_{51}H_{82}AgF_3N_2O_7S_5 \cdot CH_3CN$: C, 52.99; H, 7.13; N, 3.50. Found: C, 52.70; H, 7.24; N, 3.38. Compound **3**: yield, 77%; Λ_M (1×10^{-4} M in CH_3NO_2) 91.5 Ω^{-1} mol^{-1} cm^2. FT IR (KBr, cm^{-1}) 2924, 2853, 1627, 1607, 1302, 1251, 1209, 1175, 1021, 835, 557. Anal. Calcd for $C_{50}H_{82}AgF_6N_2O_4PS_4$: C, 51.90; H, 7.15; N, 2.42. Found: C, 51.48; H, 7.05; N, 2.28. ^{1}H and ^{13}C NMR signals were observed at chemical shift values similar to those of **2**.

Crystal Structure Determination. Colorless crystals of [Ag(**1**)][PF_6] were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex stored at 4 °C. The data were collected at 22 °C on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Reflections collected using the ω-scan method to a maximum 2θ of 45. The crystal showed no significant intensity decay during data collection as judged by two standards measured every 148 reflections. The structure was solved by the Patterson method and refined using full-matrix least-squares techniques of the SHELXTL PLUS structure analysis package.[17] In the final cycles of refinement only the silver, sulfur, nitrogen, oxygen, phosphorus, and fluorine atoms were assigned anisotropic thermal parameters. H atoms were included in their calculated positions. This resulted in a final R (R_w) value of 0.062 (0.059) for 2383 unique reflections with $I > 3\sigma(I)$ and 363 parameters. A goodness-of-fit calculation resulted in a value of 1.38.

Table 1. Crystallographic Data for [Ag(1)][PF_6]

formula	$C_{50}H_{82}AgF_6N_2O_4PS_4$
fw	1156.3
space group	$P\bar{1}$
a, Å	9.278(2)
b, Å	11.527(3)
c, Å	27.588(7)
α, deg	100.66(2)
β, deg	90.20(2)
γ, deg	92.99(2)
V, Å^3	2896(1)
Z	2
ϱ_{calcd}, g cm^3	1.326
cryst size, mm	0.18 × 0.16 × 0.06
μ(Mo Kα), cm^{-1}	5.8
λ, Å	0.71073
temp,×a1°C	22
no. of data collected	8289 (h, k, l)
no. of unique data	7602
no. of data observed	2383 [$I > 3\sigma(I)$]
no. of variables	363
R[a]	0.062
R_w[a]	0.059

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(F) + 0.0008F^2$.

Further details of crystal data collection and refinement are summarized in Table 1. Atomic positional parameters are listed in Table 2 and selected bonding parameters are given in Table 3.

Results and Discussion

Synthesis and Mesomorphic Behavior. The macrocyclic ligand **1** smoothly reacts in dichloromethane−acetonitrile with silver salts AgX (X = CF_3SO_3, PF_6) affording colorless solutions, from which white, air- and light-stable complexes [Ag(**1**)][X] (X = CF_3SO_3 (**2**), PF_6 (**3**)) could be obtained in high yields. No side products were detected by spectroscopic means. Compounds **2** and **3** are very soluble in acetonitrile, nitromethane, or chlorinated solvents, slightly soluble in diethyl ether but insoluble in water. Spectroscopic characterization of the complexes confirmed the presence of only one complexed species whose solution structure must be akin to that of the copper(I) analogue.[11]

Whereas ligand **1** is devoided of mesomorphism, either **2** or **3** shows a single mesophase above the

(17) SHELXTL PLUS Version 4.21, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1990.

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³)[a,b] for [Ag(1)][PF₆]

	x	y	z	U_{eq}
Ag(1)	433(1)	3226(1)	1201(1)	60(1)
S(1)	2850(5)	3471(4)	1599(2)	68(2)
S(2)	1569(5)	4459(4)	550(2)	62(2)
S(3)	−2230(4)	3281(4)	1104(2)	54(2)
S(4)	185(5)	1136(4)	605(2)	65(2)
N(1)	−1060(12)	6032(10)	1091(5)	51(6)
N(2)	1440(13)	828(11)	1676(5)	58(6)
O(1)	146(13)	7086(10)	1750(4)	87(6)
O(2)	1147(12)	2361(12)	2283(4)	94(6)
O(3)	−4583(16)	4641(12)	2933(5)	107(7)
O(4)	−5081(12)	314(10)	2546(5)	89(6)
C(1)	3842(17)	4349(14)	1227(6)	69(5)
C(2)	3429(16)	4166(15)	678(6)	69(5)
C(3)	1558(16)	6035(13)	821(6)	68(5)
C(4)	40(17)	6459(15)	780(6)	70(5)
C(5)	−2382(16)	5476(13)	851(6)	55(5)
C(6)	−2339(16)	4166(12)	630(5)	56(5)
C(7)	−2699(17)	1807(14)	758(6)	73(6)
C(8)	−1619(16)	1269(15)	378(6)	71(6)
C(9)	−219(19)	−15(16)	974(7)	98(7)
C(10)	961(18)	−175(15)	1311(6)	71(5)
C(11)	2995(18)	1149(15)	1688(6)	74(6)
C(12)	3525(17)	2000(13)	1377(6)	69(5)
C(13)	−904(20)	6422(16)	1592(8)	59(5)
C(14)	−1948(17)	6044(14)	1938(6)	54(5)
C(15)	−3372(17)	6357(14)	1981(6)	64(5)
C(16)	−4316(19)	5918(15)	2317(6)	70(5)
C(17)	−3766(22)	5152(18)	2600(8)	89(6)
C(18)	−2319(20)	4943(16)	2586(7)	88(6)
C(19)	−1430(20)	5353(15)	2253(6)	80(6)
C(20)	−6084(20)	4818(17)	2963(7)	89(7)
C(21)	−6715(20)	3926(17)	3253(7)	108(7)
C(22)	−8309(20)	4048(17)	3326(7)	106(7)
C(23)	−9034(20)	3032(17)	3539(7)	109(7)
C(24)	−10611(21)	3095(19)	3593(8)	117(8)
C(25)	−11447(23)	2112(20)	3762(8)	138(9)
C(26)	−13032(22)	2204(19)	3826(8)	124(8)
C(27)	−13796(24)	1275(20)	4035(9)	142(9)
C(28)	−15343(25)	1473(22)	4142(9)	165(11)
C(29)	−16138(24)	568(24)	4392(10)	193(12)
C(30)	−17671(25)	965(24)	4493(12)	227(14)
C(31)	−18403(37)	108(31)	4777(14)	476(37)
C(32)	590(20)	1459(18)	2037(7)	65(6)
C(33)	−870(17)	1032(15)	2115(6)	58(5)
C(34)	−1906(17)	1893(15)	2176(5)	63(5)
C(35)	−3287(18)	1578(15)	2313(6)	68(5)
C(36)	−3696(20)	466(17)	2415(6)	71(5)
C(37)	−2651(18)	−369(16)	2351(6)	75(6)
C(38)	−1264(17)	−102(15)	2193(6)	67(5)
C(39)	−5526(20)	−782(17)	2667(7)	97(7)
C(40)	−7090(20)	−739(18)	2790(8)	112(7)
C(41)	−7732(20)	−1721(17)	3015(7)	104(7)
C(42)	−9322(19)	−1621(16)	3134(7)	94(7)
C(43)	−9977(19)	−2456(17)	3448(7)	97(7)
C(44)	−11539(19)	−2239(17)	3563(7)	93(6)
C(45)	−12198(20)	−3036(17)	3882(7)	106(7)
C(46)	−13788(20)	−2816(17)	3980(7)	111(7)
C(47)	−14455(20)	−3634(18)	4296(7)	111(7)
C(48)	−16042(21)	−3423(19)	4395(8)	123(8)
C(49)	−16728(26)	−4255(23)	4712(10)	176(11)
C(50)	−18313(26)	−4000(23)	4777(9)	206(13)
P(1)	5243(6)	8250(5)	656(3)	75(3)
F(1)	3629(12)	8394(11)	552(5)	148(7)
F(2)	5472(14)	9554(10)	914(6)	172(8)
F(3)	5009(12)	6909(10)	394(5)	142(7)
F(4)	6830(12)	8064(10)	750(8)	205(11)
F(5)	4782(18)	7850(14)	1120(5)	190(10)
F(6)	5679(18)	8582(15)	171(6)	201(10)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] U values are given in the form of the isotropic equivalent thermal parameter $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

melting transition. The transition temperatures and optical textures were investigated by hot-stage polarizing microscopy and differential scanning calorimetry (DSC). Compound **2** slowly melts above 50 °C to a viscous, birefringent phase whose mobility increases with temperature. Clearing occurs at 124 °C (DSC peak centered at 118 °C, ΔH = 0.88 kJ mol^{-1}), and a fan-shaped focal-conic texture develops on cooling the isotropic liquid (ΔH = −0.68 kJ mol^{-1}). Compound **3** shows a similar thermotropic behavior although it is less thermally stable. Melting slowly occurs around 70 °C giving rise to a very broad DSC peak (Figure 2). Clearing at 160 °C (ΔH = 1.36 kJ mol^{-1}) is always accompanied by slight decomposition. A glassy mesophase is obtained on cooling the isotropic liquid of both complexes to room temperature.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Ag(1)][PF₆]

Bond Distances			
Ag(1)−S(1)	2.474(5)	Ag(1)−S(2)	2.674(5)
Ag(1)−S(3)	2.490(4)	Ag(1)−S(4)	2.652(4)
S(1)−C(1)	1.795(17)	S(1)−C(12)	1.836(16)
S(2)−C(2)	1.821(16)	S(2)−C(3)	1.832(15)
S(3)−C(6)	1.807(16)	S(3)−C(7)	1.819(15)
S(4)−C(8)	1.809(16)	S(4)−C(9)	1.840(21)
N(1)−C(4)	1.459(21)	N(1)−C(5)	1.451(18)
N(2)−C(11)	1.470(20)	N(2)−C(10)	1.434(20)
C(1)−C(2)	1.534(22)	C(3)−C(4)	1.525(22)
C(5)−C(6)	1.524(19)	C(7)−C(8)	1.523(22)
C(9)−C(10)	1.475(25)	C(11)−C(12)	1.484(25)
Bond Angles			
S(1)−Ag(1)−S(2)	86.3(2)	S(1)−Ag(1)−S(3)	159.6(2)
S(2)−Ag(1)−S(3)	105.5(2)	S(1)−Ag(1)−S(4)	108.9(2)
S(2)−Ag(1)−S(4)	97.5(1)	S(3)−Ag(1)−S(4)	86.3(1)
C(1)−S(1)−C(12)	101.6(7)	C(2)−S(2)−C(3)	100.6(7)
C(6)−S(3)−C(7)	101.5(7)	C(8)−S(4)−C(9)	98.7(8)
C(4)−N(1)−C(5)	117.5(13)	C(10)−N(2)−C(11)	116.0(12)
S(1)−C(1)−C(2)	117.4(11)	S(2)−C(2)−C(1)	115.0(11)
S(2)−C(3)−C(4)	109.4(10)	N(1)−C(4)−C(3)	116.9(14)
N(1)−C(5)−C(6)	116.0(12)	S(3)−C(6)−C(5)	111.4(10)
S(3)−C(7)−C(8)	117.0(11)	S(4)−C(8)−C(7)	116.3(11)
S(4)−C(9)−C(10)	114.2(13)	N(2)−C(10)−C(9)	117.5(15)
N(2)−C(11)−C(12)	117.8(15)	S(1)−C(12)−C(11)	110.9(11)

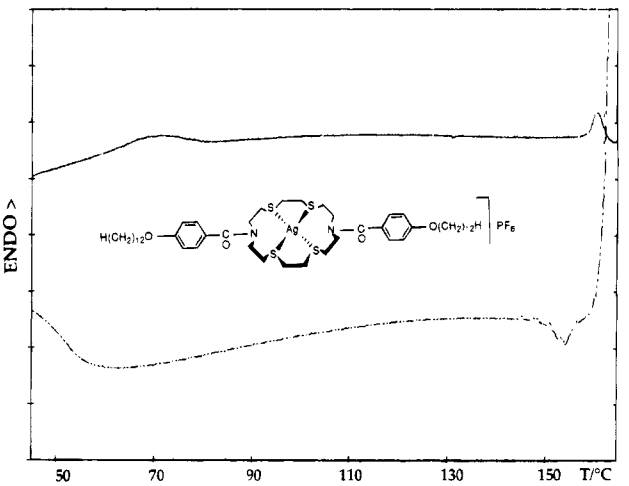

Figure 2. DSC curves for [Ag(**1**)][PF₆]. Solid and broken lines are the heating and cooling cycle, respectively. Heating rate was 10 °C/min.

X-ray Molecular Structure of [Ag(1)][PF₆]. Compound **3** was subjected to a solid-state structure analysis. The unit cell contains two [Ag(**1**)]$^+$ cations and two PF_6^- anions. A perspective view of the [Ag(**1**)]$^+$ cation is shown in Figure 3. Selected bond distances and angles are found in Table 3.

Macrocycle **1** acts as a tetradentate ligand encapsulating the silver ion by means of all sulfur atoms. The

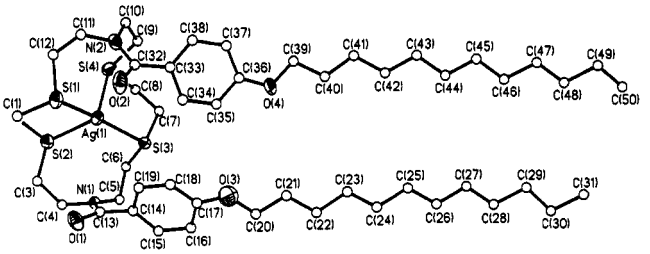

Figure 3. Perspective view of the cation of **3**, [Ag(**1**)][PF_6], with the numbering scheme. Thermal ellipsoids drawn at the 30% probability level and remaining atoms shown as uniform, arbitrarily sized circles. Hydrogens omitted for the sake of clarity.

geometry about silver is that of a flattened tetrahedron, wherein the S–Ag–S angles for the five-membered chelate rings are 86.3(2)° and 86.3(1)° and the corresponding values for the eight-membered chelate rings are 105.5(2)° and 108.9(2)°. The remaining bonding parameters of the inner core are similar to those found in related complexes with homoleptic pseudotetrahedral AgS_4 coordination spheres.[18]

The most remarkable solid-state feature of complex **3** is the lipid-like, "horseshoe" shape of the cation which brings about a supramolecular layered structure,[19,20] wherein PF_6^- anions are sandwiched between two layers of cations with fully extended chains (Figure 4). The overall bilayer structure results from stacking along the x and y axes of the successive sandwiches which affords intra- and intercation chain-to-chain interactions of similar degree. Severe tilting of the hydrocarbon chain axes with respect to the normal to the layers (Figure 5) leads to a bilayer thickness of 27.1 Å.

Mesophase Structure. The observed segregation of polar and apolar regions in the crystalline state could help to explain the mesomorphic behavior of **2** and **3**. To get useful information on the mesophase structure, the highly viscous mesophases of **2** and **3** were investigated by low-resolution X-ray diffraction on oriented samples. The XRD patterns are similar to those of the mesophases of the copper complexes previously studied.[11] The organization is mainly lamellar, the normal to the layer planes being perpendicular to the stretching direction. Beside the reflections by the layer structure (two orders of reflection), another sharp spot of very weak intensity characterizes an in-plane modulation. The layer thickness is 36 Å for both the two salts **2** and **3**; the in-plane periodicity of 60 Å was measured only for compound **2**. A diffuse ring with a maximum intensity around $q = 2\pi/4.5$ Å is a proof of the disordered intralayer organization at a molecular scale.

On the basis of the presumptive rodlike shape and in the absence of any crystalline structural information, we have previously proposed a model of an undulated monolayer smectic A phase for the copper complexes.[11] In the present case, by comparison with the crystalline state a bilayer structure (similar to those of lyotropic systems) can be proposed as well. The apparent length of complex **3** (as deduced from the crystal structure analysis) is at least 26 Å and its volume is equal to half the unit cell volume (i.e., 1448 $Å^3$). If we propose a bilayer model for the mesophase organization without imbrication of chains, the molecular length should be considerably smaller (18 Å), and since this decrease is mainly that of the hydrocarbon chains, the length of the chains must be reduced by a factor of 2. Assuming a molar volume in the mesophase of about 1500–1600 $Å^3$, the chain area should be equal to 42–44 $Å^2$. Noteworthy, the molecular dimensions are consistent with a structure in which the chains of the two half-layers are interdigitated and in extended conformation. Simultaneously, the chain area would be reduced to ca. 22 $Å^2$ for the silver complexes (and to ca. 20 $Å^2$ for the copper complexes). However, a chain area of ca. 20 $Å^2$ is consistent with a higher degree of intralayer organization. In fact, taking into account the width of the outer angle ring, we have to consider each paraffinic sublayer as a fluid where the position of a given methylene group widely fluctuates in such a way that a regular array of parallel rigid interdigitated chains, as in some lyotropic phases,[21] is excluded. Nevertheless, two adjacent paraffinic sublayers could be partially imbricated.

Another interesting point is the lyotropic behavior of these systems. By a controlled evaporation of the solvent from dilute solutions of compound **2** in acetonitrile, we were able to obtain mesogenic binary mixtures. Four different mixtures were obtained with a weight concentration between 15 and 35%.[22] However, at room temperature the mesophase is stable for solutions with 15, 18.5, and 20 wt % acetonitrile, while the isotropic phase and the mesophase coexist with 35% solvent. Whereas the viscosity decreases slightly as the amount of solvent is increased, the layer spacing increases and reaches a maximum value of 37.5 Å for 20 wt % solvent. The layer thickness does not show a further increment between 20 and 35 wt % acetonitrile. The corresponding chain area (49 $Å^2$) is slightly above the chain area in the thermotropic mesophase of the anhydrous compound. Consequently, acetonitrile swelling increases simultaneously the distances between next-neighbor polar heads in directions parallel to the layer plane and perpendicular to it.

A last point is the existence of the intralayer modulation. In lyotropic lamellar phases[23] two kind of intralayer modulations have been observed. In fluid lamellar phases the lamellae break in parallel ribbons sitting at the nodes of a 2-D centered rectangular lattice. Going from the center of the ribbons toward the edges, the chains are in a more and more disordered conformation. Starting from a L_β or a $L_{\beta'}$ phase (tilted version of L_β), it is possible to obtain a second modulated layer

(18) (a) Küppers, H. J.; Wieghardt, K.; Tsay, Y. H.; Krüger, C.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 575. (b) Stephan, D. W. *Organometallics* **1991**, *10*, 2037. (c) de Groot, B.; Loeb, S. J. *Inorg. Chem.* **1991**, *30*, 3103. (d) Nadasdi, T. T.; Stephan, D. W. *Organometallics* **1992**, *11*, 116.

(19) See for example: (a) Ciajolo, M. R.; Corradini, P.; Pavone, V. *Gazz. Chim. Ital.* **1976**, *106*, 807; *Acta Crystallogr.* **1977**, *B33*, 553. (b) Landi, E.; Salerno, V.; Vacatello, M. *Gazz. Chim. Ital.* **1977**, *107*, 27. (c) Kind, R.; Plesko, S.; Arend, H.; Blinc, R.; Zeks, B.; Seliger, J.; Lozar, B.; Slak, J.; Levstik, A.; Filipic, C.; Zagar, V.; Lahajnar, G.; Milia, F.; Chapuis, G. *J. Phys. Chem.* **1979**, *71*, 2118. (d) Okuyama, K.; Watanabe, H.; Shimomura, M.; Hirabayashi, K.; Kunitake, T.; Kajiyama, T.; Yasuoka, N. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3351.

(20) Layered structures with alternating polar and nonpolar layers also occur for neutral species. Menger, F. M.; Lee, J.-J.; Hagen, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 4017 and references therein.

(21) (a) Skoulios, A. *Adv. Colloid Interface Sci.* **1967**, *1*, 79. (b) Luzzati, V. In *Biological Membranes*; Chapmann, D., Ed.; Academic Press: New York, 1968.

(22) In fact, owing to our method of preparation, the concentration of these mixtures is not known with a good accuracy (±3%).

(23) Charvolin, J.; Tardieu, A. In *Solid State Physics*; Ehrenreich, H.; Seitz, F., Turnbull, D., Eds.; Academic Press: New York, 1978; Supplement 14, p 209.

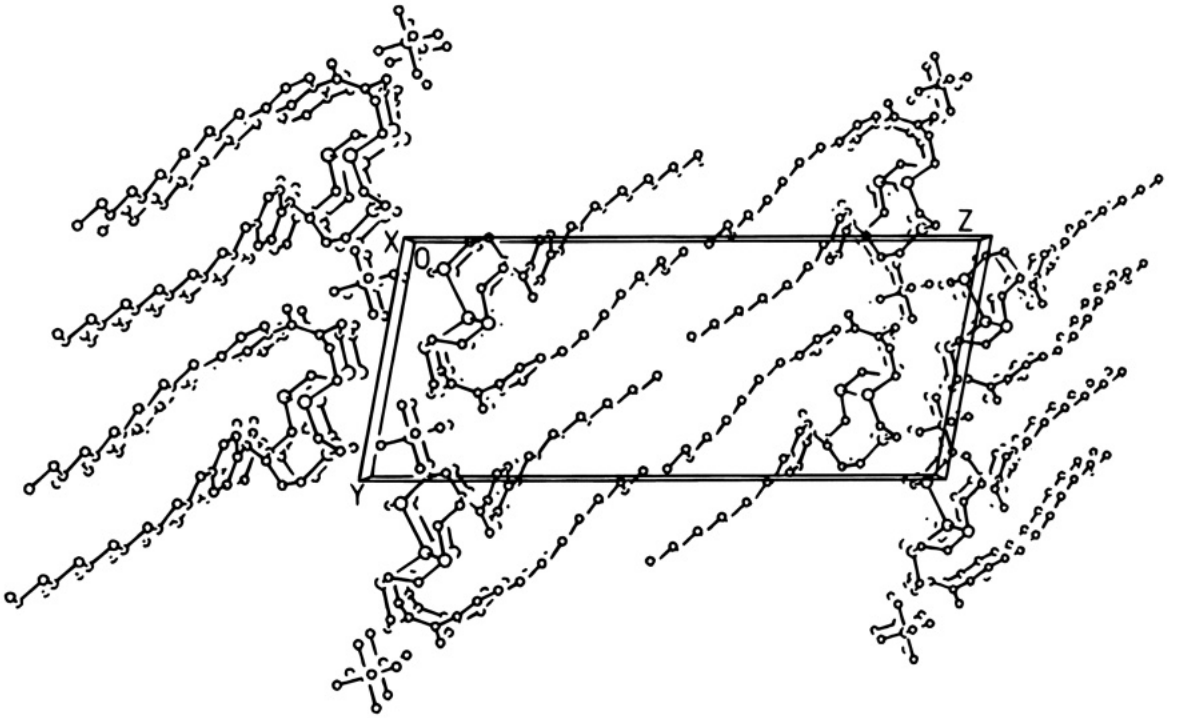

Figure 4. Crystal packing of **3** down the x axis.

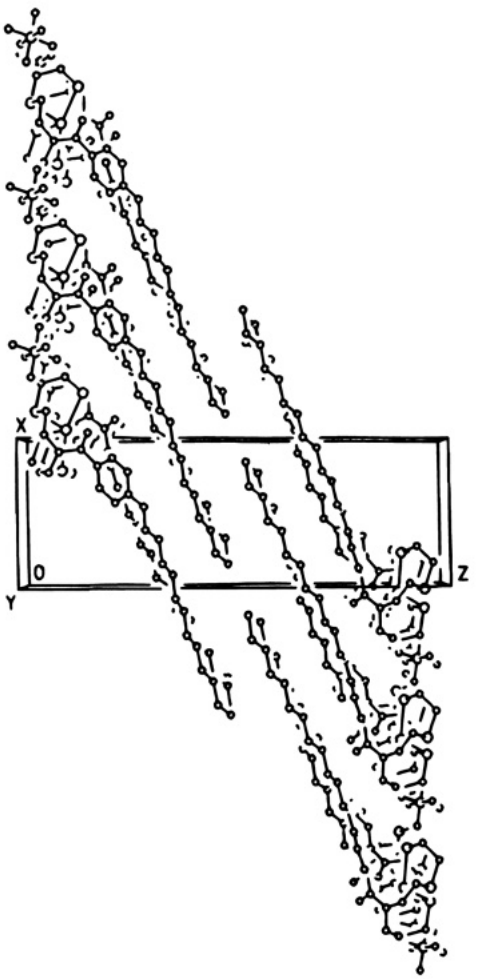

Figure 5. Crystal packing of **3**: view down the y axis of two rows in the bilayer.

structure, the so-called ripple phase $P_{\beta'}$, with an oblique lattice and in which the chains are in an all-trans conformation while the interfaces between the different sublayers are rippling with a global monoclinic symmetry.

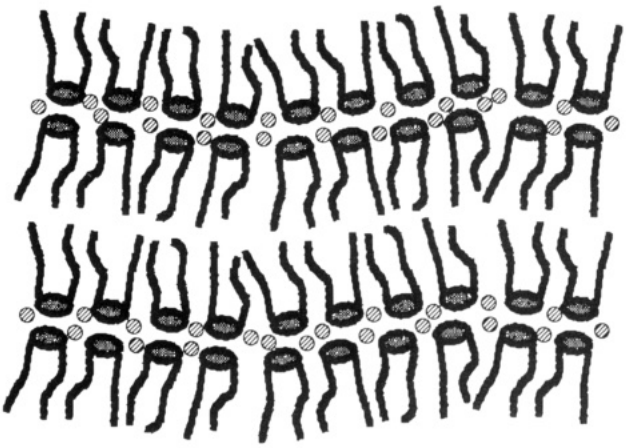

Figure 6. Schematic representation of the modulated bilayered structure of the mesophase. The anions are represented by hatched small circles.

Our XRD pattern of aligned samples cannot fit with a centered rectangular lattice, taking into account the positions of the different reflections. We have proposed a simple rectangular lattice,[11] but in fact given the relatively poor quality of our alignement we cannot exclude an oblique lattice. Indeed a tilt of the long hydrocarbon chains could reduce the hydrocarbon sublayer thickness in a larger amount than a simple melting. Therefore our lamellar phase is a ripple phase, but we do not know if the symmetry of the phase is orthorhombic or monoclinic. However, in this phase the chains are molten and therefore only the positions of the rigid ionic moiety of the complexes are affected by the modulation (Figure 6).

This fact explains also the very weak intensity of the spot characterizing the modulation compared to the first order of reflection on the lamellar planes. Moreover, we were not able to put in evidence any extra ring

characteristic of a modulation in lyotropic mixtures, therefore, the modulation could disappear as the distance between the molecules is increased.

Conclusions

A comparison between the structure of the crystalline phase and that of the mesophase of the silver complexes allows us to give a description of the molecular conformation: (a) the molecules have a U shape and form a bilayer structure in the mesophase in such a way that the two hydrocarbon chains belonging to the same molecule point in the same direction; (b) the chains are in a disordered conformation and their area in a plane parallel to the layers is about 44 $Å^2$; (c) an undulation of small amplitude of the ionic sublayer is at the origin of the 2-D periodic structure and could explain the high viscosity of this mesophase.

In summary, we have shown that metal-promoted self-aggregation of nonmesogenic macrocyclic ligands can afford bilayered structures which exhibit both thermotropic and lyotropic mesomorphism. On the basis of their organization at the molecular and supramolecular level, the amphiphilic silver complexes (but the same argument could be extended to the analogous copper complexes) can be seen as inorganic analogues of lipids, and their unique structural features call for possible interesting properties (for example, monolayers, Langmuir–Blodgett films, or vescicles formation).

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Supplementary Material Available: Details of the crystal structure of **3** including data collection parameters, complete bond distances and angles, anisotropic thermal parameters, hydrogen atom positions, and selected torsion angles (10 pages); listing of observed and calculated structure factors for **3** (28 pages). Ordering information is given on any current masthead page.

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