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Ionic metallomesogens derived from silver(I) bis-amine complexes: Structure and mesogenic behavior

María del Carmen Lequerica [1], María Jesús Baena [2], Pablo Espinet *,[1]

IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47071 Valladolid, Spain

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Abstract

Complexes $[Ag(NH_2R)_2]X$, ($X = NO_3$, $R = –C_6H_4–C_nH_{2n+1}$-*p*, $–C_6H_4–O–C_nH_{2n+1}$-*p*, $–CH_2–C_6H_4–O–C_nH_{2n+1}$-*p*, $n = 6, 8, 10, 12, 14$; $X = BF_4$, $R = –CH_2–C_6H_4–O–C_nH_{2n+1}$-*p*, $n = 6, 8, 10, 12, 14$; $X = OAc$, $R = –CH_2$-$C_6H_4–O–C_{10}H_{21}$-*p*; $X = CF_3SO_3$, $R = –CH_2–C_6H_4–O–C_{10}H_{21}$-*p*) have been prepared. They all show S_A mesophases corresponding to two kinds of structures, already present in the solid state. The alkylaniline and alkoxyaniline derivatives adopt a bilayered structure where the cation has an extended centrosymmetric conformation. The benzylamine derivatives contain U-shaped cations giving rise to a bilayered structure which allows microsegregation of the organic part of the molecule from the inorganic Ag···(anion) part. Some degree of interdigitation of the terminal chains is observed for all the complexes with aryl containing ligands.

Keywords: Liquid crystals; Metallomesogens; Bilayered mesophases; Silver complexes; Amine complexes

1. Introduction

Ionic mesogens are among the first liquid crystals systematically studied [1]. They combine the inherent properties of liquid crystals and those of the ionic compounds, and have been used as ordered solvents, as catalysts and templates for synthesis, as optical and ferroelectric systems, as electronic or ionic conductors, and as membranes [2]. The term "ionic metallomesogens" refers to mesogens based on ionic molecules bearing a transition metal. Examples can be found in several reviews [2b,3]. In general, much attention has been paid to complexes with heterocyclic N-donor ligands, such as mono and poly-substituted stilbazole silver complexes [4], pyridine carboxylates and pyridine imine silver complexes [5].

Previously we have published studies on ionic metallomesogens,[6] including silver amino complexes with *n*-alkylamines, $[Ag(NH_2–C_nH_{2n+1}$-$n)_2]X$, ($X = NO_3$, BF_4, OAc) that are a very much related to this paper [7]. The compounds displayed a thermotropic lamellar mesophase corresponding to a bilayered arrangement of U-shaped $[Ag(NH_2–C_nH_{2n+1}$-$n)_2]^+$ cations sandwiching a layer of anions. This kind of structure is reminiscent of that of the biomembranes and can be found in other mesogenic ionic systems [8]. In this work, we extend our study to silver primary amine complexes with a rigid part in the amine ligand (anilines and benzylamines) and alkyl or alkoxy terminal chains (series **1**–**4**). Complexes with different anions were prepared for the benzylamine series (compounds **5** and **6**) in order to test the anion influence on the properties of the material. The complexes are labeled according to the series they pertain and the length of the alkyl chain, as follows:

Series **1**: $[Ag(NH_2–C_6H_4–C_nH_{2n+1}$-$p)_2](NO_3)$
$n = 6, 8, 10, 12, 14$
Series **2**: $[Ag(NH_2–C_6H_4–O–C_nH_{2n+1}$-$p)_2](NO_3)$
$n = 6, 8, 10, 12, 14$

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* Corresponding author. Tel./fax: +34 983 423 231.
E-mail address: espinet@qi.uva.es (P. Espinet).

[1] Facultad de Ciencias.

[2] E. T. S. de Ingenieros Industriales.

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Series 3: $[Ag(NH_2–CH_2–C_6H_4–O–C_nH_{2n+1}p)_2](NO_3)$
$n = 6, 8, 10, 12, 14$
Series 4: $[Ag(NH_2–CH_2–C_6H_4–O–C_nH_{2n+1}\text{-}p)_2](BF_4)$
$n = 6, 8, 10, 12, 14$
Compound 5: $[Ag(NH_2–CH_2–C_6H_4–O–C_{10}H_{21}\text{-}p)_2](OAc)$
Compound 6: $[Ag(NH_2–CH_2–C_6H_4–O–C_{10}H_{21}\text{-}p)_2]$
(CF_3SO_3)

2. Experimental

2.1. General

Experimental procedures, analytical and spectroscopic determinations, and optical and thermal mesophase studies, were as reported in reference 7. A Phillips Analytical diffractometer equipped with a PW1710 generator was used for the X-ray powder diffraction in solid state, using monochromatic Cu Kα radiation ($\lambda = 1.54$ Å). The samples were held on a rectangular 20 × 15 mm aluminium sample holder. The X-ray scanned from 3° to 70° 2θ. XRD measurements in the mesophase were carried out with a Philips X'Pert PRO MPD X-ray diffractometer in th-th configuration equipped with a PW3373 generator and a high temperature chamber (Anton Paar HTK1200). Monochromatic Cu Kα radiation ($\lambda = 1.54$ Å) was used, and the samples were held on circular 18 mm diameter and 0.4 mm depth alumina sample holder coated with aluminium foil. Three diffractograms were taken for each sample: the first at 25 °C in the solid state, the second 10 °C over the melting point and the third 10 °C under the clearing point. The X-ray area scanned from 2° to 50° 2θ. Solvents were dried and distilled prior to use. The silver salts and the 4-*n*-alkylanilines were obtained from commercial sources and used without further purification.

2.2. Computational methods

Calculations were carried out at the HF level of theory as implemented in the GAUSSIAN 98.11 program [9]. Due to the existence of an Ag atom a quasi-relativistic pseudopotential (LANL2DZ, Los Alamos potential) was used where the basis functions for the valence s and p electrons consist of the standard double-z basis set (notation HF/LANL2DZ). Schematic representations of the structures were obtained and analyzed by using the Spartan 4:1 program [10].

2.3. Preparation of ligands and complexes

Literature procedures were used to synthesize 4-*n*-alkoxyanilines [11], 4-*n*-alkoxybenzonitriles[12] and 4-*n*-alkoxybenzylamines [13], although in this last case a small variation on the method was introduced as specified below.

2.3.1. Preparation of 4-n-alkoxybenzylamines $H_{2n+1}C_nO–C_6H_4–CH_2NH_2$ ($n = 6–14$)

To a suspension of 0.66 g (17.4 mmol) of $LiAlH_4$ in 40 mL of dry diethylether under nitrogen atmosphere was added dropwise a solution of 4.5 g (17.4 mmol) of the corresponding 4-*n*-alkoxybenzonitrile in 20 mL of diethylether. The mixture was stirred for 1/2 h. Then, the flask was cooled in an ice bath and water was added slowly to destroy the excess of $LiAlH_4$, followed by 15 mL of H_2SO_4 6 N. The mixture was cleaned with 4 × 15 mL of diethylether, the aqueous solution was cooled to 5 °C and NaOH pellets were slowly added until ca. pH 11. The basic solution was diluted with water (10 mL) and extracted with diethylether (4 × 15 mL). The organic phases were collected together, dried over anhydrous magnesium sulfate, filtered off and evaporated to dryness. The amine was purified by column chromatography with silica as stationary phase and a mixture of $CHCl_3$/EtOH (10:1) as eluent. Yield: 65–70%. Elemental *Anal.* Calc. for $n = 6$: C, 73.32; H, 10.21; N, 6.76. Found: C, 73.58; H, 9.90; N, 6.51%. *Anal.* Calc. for $n = 8$: C, 76.55; H, 10.71; N, 5.95. Found: C, 76.90; H, 10.24; N, 5.72%. *Anal.* Calc. for $n = 10$: C, 77.51; H, 11.10; N, 5.32. Found: C, 77.78; H, 11.41; N, 4.81%. *Anal.* Calc. for $n = 12$: C, 78.29; H, 11.41; N, 4.81. Found: C, 78.01; H, 10.93; N, 4.57%. *Anal.* Calc. for $n = 14$: C, 78.94; H, 11.67; N, 4.38. Found: C, 78.54; H, 11.22; N, 4.10%. Spectroscopic data are for $n = 10$: ν_{max} (KBr)/cm^{-1}: 3280br. δ_H (300 MHz; $CDCl_3$; Me_4Si): 7.21 (2H), 6.86 (2H, AA′XX′ spin system, *J* 8.7, aromatic hydrogens) 3.94 (2H, t, *J* 6.6, $–O–CH_2$-) 3.79 (2H, s, $–Ph–CH_2–N$); 1.51 (2H, br s $–NH_2$) 1.81–0.86 (m, alkyl chain).

2.3.2. Preparation of $[Ag(NH_2–C_6H_4\text{-}n\text{-}C_nH_{2n+1})_2](NO_3)$

To a solution of $AgNO_3$ (0.255 g, 1.5 mmol) in acetonitrile (ca. 15 mL), shielded from light, was added the corresponding amine (3 mmol) and the mixture was stirred at room temperature for 4 h. The resulting solution ($n = 6$, 8, 10) or white suspension ($n = 12$, 14) was concentrated under vacuum and cooled overnight in the freezer. The crystallized white product was collected by filtration, washed with diethyl ether and dried under vacuum. The products were further purified by recrystallization from acetonitrile/diethyl ether. Yields: 52–87%. Elemental *Anal.* Calc. for $n = 6$: C, 54.97; H, 7.30; N, 8.01. Found: C, 54.95; H, 7.28; N, 8.05%. *Anal.* Calc. for $n = 8$: C, 57.93; H, 7.99; N, 7.24. Found: C, 57.90; H, 7.95; N, 7.25%. *Anal.* Calc. for $n = 10$: C, 60.37; H, 8.55; N, 6.60. Found: C, 60.32; H, 8.58; N, 6.68%. *Anal.* Calc. for $n = 12$: C, 62.42; H, 9.02; N, 6.07. Found: C, 62.39; H, 8.76; N, 6.09%. *Anal.* Calc. for $n = 14$: C, 64.16; H, 9.42; N, 5.61. Found: C, 64.06; H, 9.50; N 5.64%. Spectroscopic data are for $n = 10$: ν_{max}(KBr)/cm^{-1}: 3421br m, 1618m, 1517s, 1384br s. δ_H (300 MHz; $CDCl_3$; Me_4Si): 6.93 (4H), 6.81 (4H, AA′XX′ spin system, *J* 8.3, aromatic hydrogens) 4.40 (4H, v br s, $–NH_2$); 2.43 (4H, t, *J* 7.7, $–Ph–CH_2–$) 1.51–0.89 (m, alkyl chain).

2.3.3. Preparation of [Ag(NH$_2$–C$_6$H$_4$–O-n-C$_n$H$_{2n+1}$)$_2$]-(NO$_3$)

The synthetic method is the same as for the alkylaniline complexes above. For $n = 6$–10 a small amount of precipitate was formed during the reaction, which was removed. Times of reaction were shorter (2 h) than for the alkyl aniline complexes in order to reduce decomposition. Yields: 40–70%. Elemental *Anal.* Calc. for $n = 6$: C 51.80, H 6.88, N 7.55. Found: C 51.90, H 6.69, N 7.56%. *Anal.* Calc. for $n = 8$: C, 54.90; H, 7.55; N, 6.86. Found: C, 55.09; H, 7.48; N, 6.94%. *Anal.* Calc. for $n = 10$: C, 57.48; H, 8.14; N, 6.28. Found: C, 57.31; H, 7.95; N, 6.31%. *Anal.* Calc. for $n = 12$: C, 59.66; H, 8.62; N, 5.80. Found: C, 59.60; H, 8.67; N, 5.80%. *Anal.* Calc. for $n = 14$: C, 61.53; H, 9.04; N, 5.38. Found: C, 61.70; H, 8.85; N, 5.31%. Spectroscopic data are for $n = 10$: $\nu_{\max}$ (KBr)/cm^{-1}: 3346m, 3282m, 1514s, 1364br s, 1243s. δ_H (300 MHz; CDCl$_3$; Me$_4$Si): 6.85 (4H), 6.76 (4H, AA′XX′ spin system, *J* 8.8, aromatic hydrogens), 3.88 (4H, t, *J* 6.6, –O–CH$_2$–), 2.96 (4H, v br s, –NH$_2$), 1.77–0.89 (m, alkyl chain).

2.3.4. Preparation of [Ag(NH$_2$-CH$_2$–C$_6$H$_4$-O-n-C$_n$-H$_{2n+1}$)$_2$](NO$_3$)

To a suspension of the 4-*n*-alkoxybenzylamine (3 mmol) in 10 mL of acetonitrile was added a solution of AgNO$_3$ (0.255 g, 1.5 mmol) in acetonitrile. After stirring for 4 h shielded from light, the resulting suspension was concentrated ($n = 6$, 8) and then filtered off. The white solid was washed with diethyl ether. Yields: 80–85 %. Elemental analysis (%): Found: C 53.55, H 7.11, N 7.20; calc. for $n = 6$: C 53.42, H 7.24, N 7.19. Found: C 56.26, H 7.53, N 6.11; calc. for $n = 8$: C 56.24, H 7.87, N 6.56. Found: C 58.63, H 8.06, N 6.17; calc. for $n = 10$: C 58.61, H 8.39, N 6.03. Found: C 60.32, H 8.49, N 5.69; calc. for $n = 12$: C 60.62, H 8.84, N 5.58. Found: C 62.23, H 8.80, N 5.12; calc. for $n = 14$: C 62.36, H 9.22, N 5.19. Spectroscopic data are for $n = 10$: $\nu_{\max}$(KBr)/cm^{-1}: 3301m, 3247m, 1513s, 1368br s, 1250s, 1612m, 1584m. δ_H (300 MHz; CDCl$_3$; Me$_4$Si): 7.18 (4H), 6.83 (4H, AA′XX′ spin system, *J* 8.6, aromatic hydrogens), 3.89 (4H, t, *J* 6.6, -O-CH$_2$-), 3.77 (4H, s, –Ph–CH$_2$–N), 3.31 (4H, br s, –NH$_2$), 1.78–0.89 (m, alkyl chain).

2.3.5. Preparation of [Ag(NH$_2$-CH$_2$-C$_6$H$_4$-O-n-C$_n$H$_{2n+1}$)$_2$] BF$_4$

To a suspension of 4-*n*-decyloxybenzylamine (0.51 g, 1.94 mmol) in 10 mL of acetonitrile, shielded from light, was added a solution of AgBF$_4$ (0.97 mmol) in ca. 3 mL of acetonitrile. A white precipitate was formed and after 30 min stirring CH$_2$Cl$_2$ was added to dissolve the precipitate. The solution was filtered, concentrated, and then crystallized by cooling in the freezer. The white solid collected was washed with diethyl ether. Yields: 70–92 %. Elemental *Anal.* Calc. for $n = 6$: C, 51.25; H, 6.95; N, 4.60. Found: C, 51.15; H, 6.74; N, 4.59%. *Anal.* Calc. for $n = 8$: C, 54.15; H, 7.57; N, 4.21. Found: C, 54.08; H, 7.32; N, 4.12%. *Anal.* Calc. for $n = 10$: C, 56.60; H, 8.10; N, 3.88. Found: C, 56.55; H, 7.87; N, 4.09%. *Anal.* Calc. for $n = 12$: C, 58.69; H, 8.55; N, 3.60. Found: C, 58.60; H, 8.13; N, 3.71. *Anal.* Calc. for $n = 14$: C, 60.50; H, 8.95; N, 3.36. Found: C, 60.62; H, 8.74; N, 3.50%. Spectroscopic data are for $n = 10$: $\nu_{\max}$ (KBr)/cm^{-1}: 3347m, 3300m, 1251s, 1036br. δ_H (300 MHz; CDCl$_3$; Me$_4$Si): 7.17 (4H), 6.84 (4H, AA′XX′ spin system, *J* 8.5, aromatic hydrogens), 3.91 (4H, t, *J* 6.6 Hz, –O–CH$_2$–), 3.78 (4H, s, –Ph–CH$_2$–N), 2.91 (4H, br s, –NH$_2$), 1.81–0.86 (m, alkyl chain).

2.3.6. Preparation of [Ag(NH$_2$-CH$_2$-C$_6$H$_4$–O-n-C$_{10}$H$_{21}$)$_2$]-(OAc)

The synthetic method was the same as for the BF$_4$ complex above described. Yield: 47%. Elemental *Anal.* Calc.: C, 62.33; H, 8.86; N, 4.03. Found: C, 62.48; H, 8.77; N, 4.07%. $\nu_{\max}$ (KBr)/cm^{-1}: 3448br, 1578s, 1513s, 1249s. δ_H (300 MHz; CDCl$_3$; Me$_4$Si): 7.21 (4H), 6.86 (4H, AA′XX′ spin system, *J* 8.6, aromatic hydrogens), 3.94 (4H, t, *J* 6.5, –O–CH$_2$–); 3.79 (4H, s, –Ph–CH$_2$–N), 2.98 (4H, br s, –NH$_2$); 1.99 (3H, s, OOC-CH$_3$), 1.80–0.95 (m, alkyl chain).

2.3.7. Preparation of [Ag(NH$_2$–CH$_2$–C$_6$H$_4$–O-n-C$_{10}$H$_{21}$)$_2$]-(CF$_3$SO$_3$)

The synthetic method was the same as above. Yield: 17%. Elemental *Anal.* Calc.: C, 53.63; H, 7.46; N, 3.57. Found: C, 53.50; H, 7.22; N, 3.61%. $\nu_{\max}$(KBr)/cm^{-1}: 3301m, 3247m, 1513m, 1251vs, 1032s. δ_H (300 MHz; CDCl$_3$; Me$_4$Si): 7.17 (4H), 6.84 (4H, AA′XX′ spin system, *J* 8.6, aromatic hydrogens), 3.91 (4H, t, *J* 6.6, –O–CH$_2$–), 3.79 (4H, s, –Ph–CH$_2$–N), 3.03 (4H, br s, –NH$_2$), 1.81-0.86 (m, alkyl chain).

3. Results and discussion

3.1. Syntheses

The complexes were prepared by stoichiometric reaction (1:2) of the silver salt AgX, (X = NO$_3$, BF$_4$, OAc, CF$_3$SO$_3$) with the correspondent amine, in acetonitrile. The products were isolated as white microcrystalline solids. They are light sensitive in long and heavy exposures.

3.2. Mesogenic behavior

Optical microscopy with polarized light revealed that all the complexes exhibit only a typical lamellar S$_A$ phase after melting, characterized by focal conic, mielinic and homeotropic textures [14]. Often (mostly in the benzylamine series and for high clearing points) the persistence of the homeotropic texture is large, and it has to be characterized by rubbing the sample. The S$_A$ mesophase for the *p*-alkyl (**1**) and *p*-alkoxyaniline (**2**) complexes is very viscous, and traces of decomposition are observed at the melting point, becoming more severe at the clearing point. Decomposition after melting was heavier in alkoxyaniline than in alkylaniline complexes and a deep red coloration was observed, probably due to the formation of oxidation products of the alkoxyaniline. Thus, for series **2**, we cannot assign the data of the S_A mesophase observed as pertaining to the starting complex, since they must be significantly altered by the mixture with appreciable amounts of the decomposition product. The *p*-alkoxybenzylamine complexes (series **3** and **4**) are far more thermally stable than aniline derivatives. Slight decomposition is observed only at the clearing point.

The phase transition temperatures and transition enthalpies, measured by differential scanning calorimetry (DSC), are collected in Table 1. Transition temperatures are plotted in Fig. 1 for easy comparison.

In general, the mesogenic behavior of the silver aniline or benzylamine complexes is similar for the four series to that found previously for aliphatic amine derivatives: only a S_A mesophase and melting points increasing with the length of the chain, higher for series **1**–**4** than for the complexes with aliphatic amines, due to the presence of aromatic and dipolar interactions. The tetrafluoroborate complexes (series **4**) show much lower melting temperatures and shorter ranges of mesophase than the nitrate homologous (series **3**). For complex **4.6** the mesophase is monotropic.

Fig. 2 compares the thermal behavior of complexes having the same cation, $[Ag(C_{10}H_{21}–O–C_6H_4–CH_2–NH_2)_2]^+$ and different anions NO_3^- (**3.10**), BF_4^- (**4.10**), OAc^- (**5**) and $CF_3SO_3^-$ (**6**) (see also Table 1). The nature, shape and volume of the anions should influence the ionic packing and the electrostatic attractive forces between ions. Consistent with the results found for *n*-alkylamines, the planar nitrates seem to allow for stronger interactions with the cations than the tetrahedral BF_4^- ions, both in the solid state and in the melt. In addition, covalent Ag–O interactions in the nitrates migh reinforce the lattice stability [8b,15]. The planar but bulkier and less symmetric OAc^- makes the interionic forces weaker, leading to a marked reduction in both melting and clearing points. The bulkiest $CF_3SO_3^-$ is not able to stabilize the mesophase after melting, although the hysteresis produced in the cooling process leads to the formation of a mesophase before crystallization occurs, observed in DSC. This monotropic mesophase extends over a range of 35 °C and was assigned a S_A structure according to the enthalpy change.

Table 1
Thermal parameters for the silver amino complexes prepared

Compound	n	Transition	T (°C)	ΔH (kJ mol^{-1})
1[a]	6	C–C′	62.2	2.5
		C′– S_A	88.5	20.2
		S_A–$I_{dec.}$	140	–
	8	C–S_A	90.0	34.5
		S_A–$I_{dec.}$[b]	135	–
	10	C–S_A	95.4	40.6
		S_A–$I_{dec.}$[b]	135	–
	12	C–S_A	101.0	57.9
		S_A–$I_{dec.}$[b]	127	–
	14	C–S_A	102.1	69.4
		S_A–$I_{dec.}$[b]	119	–
2[c]	6	C–S_A	70.2	26.2
		S_A–$I_{dec.}$[b]	144	–
	8	C–S_A	82.9	43.8
		S_A–$I_{dec.}$[b]	135	–
	10	C–S_A	87.5	57.3
		S_A–$I_{dec.}$[b]	124	–
	12	C–S_A	98.8	71.7
		S_A–$I_{dec.}$[b]	130	–
	14	C–C′	91.6	
		C′–S_A	99.6	87.5[e]
		S_A–$I_{dec.}$[b]	115	–
3[d]	6	C–C′	80.0	
		C′– S_A	83.7	33.8[e]
		S_A–I	115.2	2.2
	8	C–S_A	78.3	41.7
		S_A–I	129.1	1.7
	10	C–S_A	89.1	59.7
		S_A–I	137.1	1.2
	12	C–S_A	94.8	68.7
		S_A–I	135.4	1.1
	14	C–S_A	99.7	82.1
		S_A–I	133.5	0.8
4[d]	6	C–I	(53.7)	(30.5)
		I–S_A	43.4	−1.6
	8	C–S_A	70.7	38.0
		S_A–I	95.1	1.3
	10	C–S_A	80.9	55.5
		S_A–I	112.6	1.2
	12	C–C′	55.2	4.0
		C′–C″	59.5	0.8
		C″–S_A	83.5	52.3
		S_A–I	112.3	0.9
	14	C–S_A	89.1	72.7
		S_A–I	116.1	0.7
5[d]	10	C–S_A	39.6	54.6
		S_A–I	76.7	2.4
6[d]	10	C–C′	30.9	
		C′–I	38.7	47.3[e]
		I–S_A	15.7	−1.4

[a] Melting temperatures for the first heating.
[b] Data from the microscope.
[c] Melting temperatures for the first heating, fast run at 20 °C/min.
[d] Melting temperatures for the second heating; data in parenthesis are for the first heating.
[e] Combined enthalpies.

3.3. X-ray diffraction studies

The similarity in mesophase properties of the complexes reported here and the alkylamine complexes previously reported [7], does not imply structural similarity in the mesophase. The molecules under study can adopt different shapes considering a sp^3 hybridization for the amine nitrogen and easy rotation around single C–C, C–N, or Ag–N bonds. For aniline complexes in a U-shaped conformation the aromatic ring takes necessarily the chains of the two ligands far from each other, and it is expected that in a condensed phase the cations derived from anilines will not adopt a U-shaped conformation, which would produce a worse molecular packing than an extended conformation. However, for the bisbenzylamine complexes molecular models suggest that extended or U-shaped conformations are both compatible with a good molecular packing.

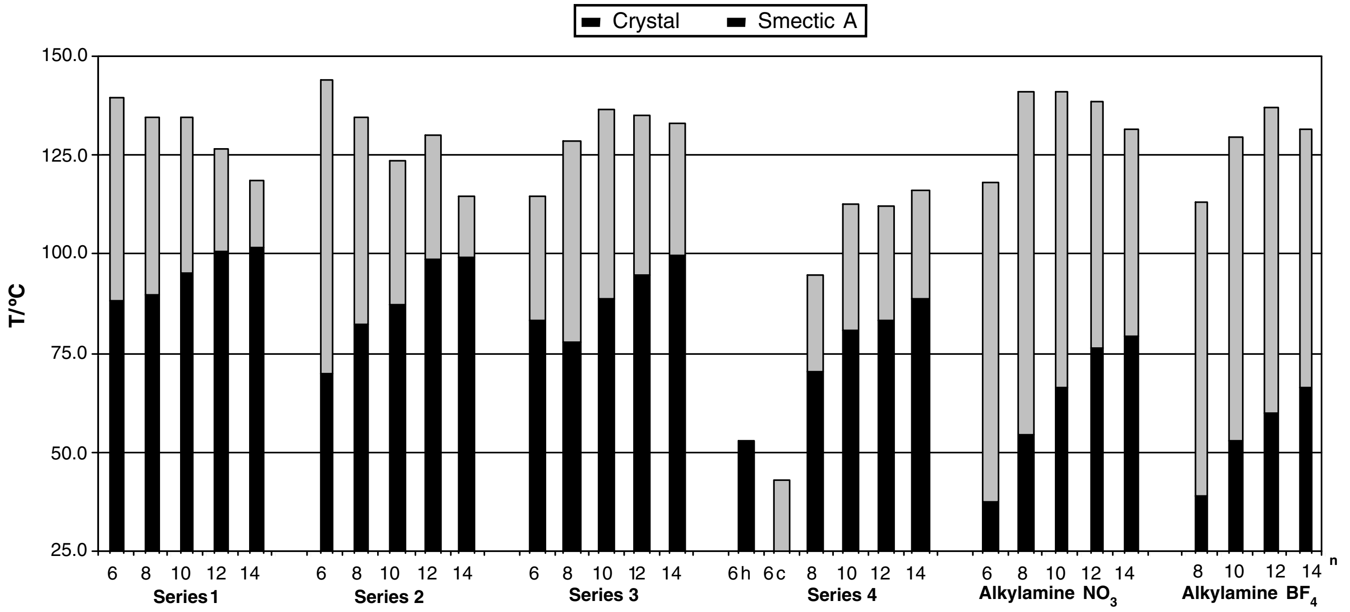

Fig. 1. Transition temperatures for the complexes (h = heating; c = cooling). Bis-*n*-alkylamine silver(I) complexes from Ref. [7] are plotted for comparison.

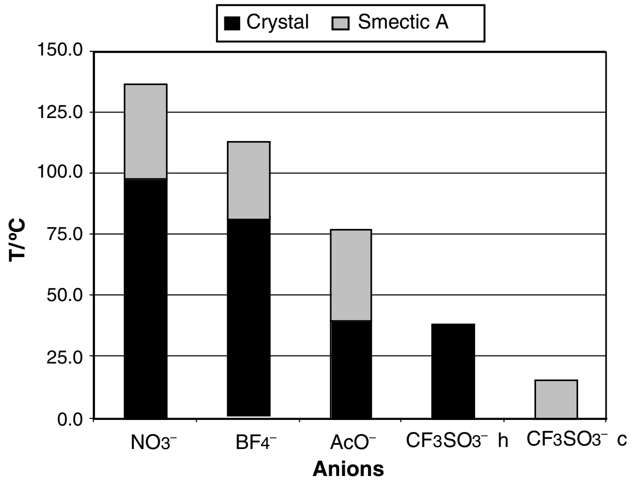

Fig. 2. Transition temperatures of the bis(4-*n*-decyloxybenzylamine) silver (I) complexes (h = heating; c = cooling).

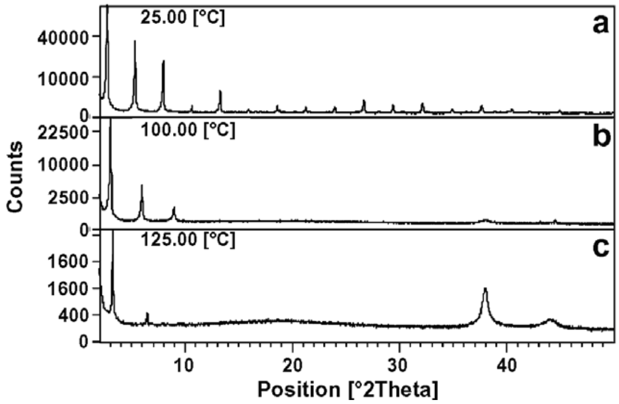

Fig. 3. Temperature dependence of the $[Ag(NH_2–C_6H_5–C_{10}H_{21})_2]NO_3$ diffractogram: (a) solid state; (b) near the melting point; (c) near the clearing point. Reflections at $2\theta = 38°$ and $44°$ arise from metallic silver planes (1 1 1) and (2 0 0), respectively [17].

Although there are exceptions [16], for simple molecular shapes and mesophases the solid state structure is frequently related to the mesophase, and is a good starting point to understand the mesogenic behavior. It was impossible to obtain single crystals of the complexes suitable for X-ray diffraction, so powder measurements were taken on polycrystalline samples. All the diffraction diagrams exhibit a simple diffraction pattern (see for instance Fig. 3a), also similar to that shown by the bis-*n*-alkylamine silver complexes, consisting of periodic reflections of (0 0 l) planes. This indicates a layered arrangement of cations with the silver centers defining a layer separated $d_{(001)}$ from the nearest equivalent silver layer. This interplanar distance should depend on how the amine ligands in a cation are arranged one respect to the other. In what follows we compare, for each series of complexes, the observed $d_{(001)}$ distance and the calculated length of the cation (L_{calc}), in order to decide the most likely cation shape in the solid state.

XRD data were also taken on the mesophases in order to see whether the arrangement in the mesophase was in fact related to the solid. Three different S_A arrangements were considered [18]: S_{A1}, when the molecules pack together in monolayers; S_{A2}, when arranged in bilayers; and S_{Ad}, when there is some interdigitation in the bilayer. All of them are characterized by a periodic XRD pattern of (00l) reflections, as observed in the high temperature diffractograms of Fig. 3b or c, but they can be distinguished by comparing the interplanar spacing with the molecular parameters. Table 2 collects $d_{(001)}$ values for the four series of complexes. They show a very good linear dependence

Table 2
Experimental interplanar spacing ($d_{(001)}$) for the series studied

Series	*n*	$d_{(001)}$ (Å)[19]
1	**6**	28.81
	8	32.70
	10	36.76
	12	40.45
	14	44.58
		$d_{(001)} = 1.01\ (2n) + 16.30$
		$r = 0.99948$
2	**7**	30.56
	9	35.27
	11	38.84
	13	43.03
	15	47.08
		$d_{(001)} = 1.02\ (2n) + 16.52$
		$r = 0.99932$
3	**7**	28.30
	9	32.77
	11	37.42
	13	42.85
	15	47.29
		$d_{(001)} = 1.20\ (2n) + 11.29$
		$r = 0.99945$
4	**7**	30.62
	9	35.25
	11	39.49
	13	43.60
	15	48.43
		$d_{(001)} = 1.10\ (2n) + 15.29$
		$r = 0.99965$

The linear adjustment the total number of carbon atoms for the two terminal chains ($2n$) is given; for alkoxy chains each oxygen counts as one member.

with the chain length. Assuming an *all-trans* conformation in the alkyl chains (although random deviations are to be expected), the slope of the line corresponds to the length per methylene group, l/CH_2. A mean value of 1.26 Å is expected for a chain orientated parallel to the line defining the molecular length,[3] while smaller values for l/CH_2 will suggest tilting of the chains.

The theoretical molecular length (L_{calc}) was taken as the distance between the terminal CH_3 groups from the minimum energy conformation calculated for an isolated cations (gas phase), which have the expected *all-trans* conformation. Fig. 4 shows the optimized conformations for one representative cation ($n = 6$) of each series. The transoid centrosymmetrical conformations calculated for the alkyl (Fig. 4a) and alkoxy (Fig. 4b) aniline complexes are in good agreement with the conformations usually observed in single crystal XRD structures of a number of related complexes lacking long chains [20]. The cisoid conformation found for the bis-benzylamine complex in the gas phase (Fig. 4c) is unusual in solid state structures of complexes lacking long chains [21]. Its calculated molecular length is somewhat shorter than for the more commonly found centrosymmetric conformation, easily accessible by rotation around the N–Ag bond [22]. We will see later that this variation is unimportant to our discussion: similarly to the case of alkylamines, which are predicted a transoid centrosymmetrical conformations in the gas phase, both kinds of complexes adopt U-saped conformations for long alkyl chains, in the solid state and in the mesophase [7].

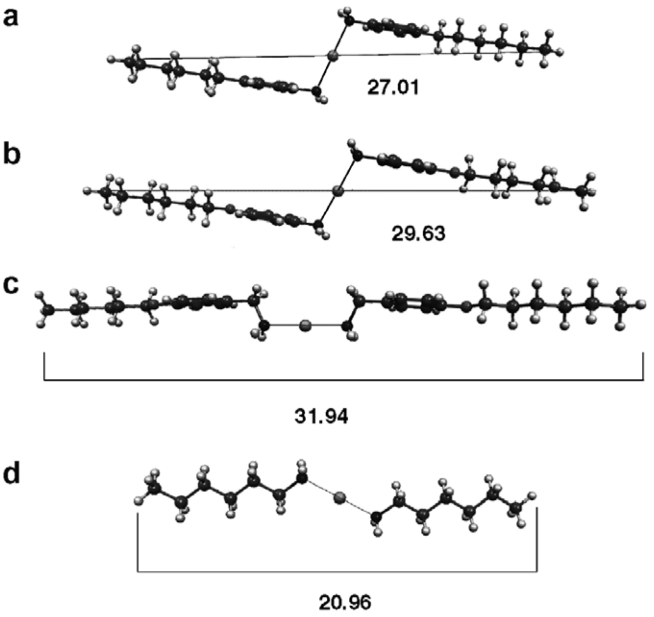

Fig. 4. Minimum energy conformation and calculated length (L_{calc}) of four representative cations. (a) $[Ag(NH_2–C_6H_4–C_6H_{13})_2]^+$. (b) $[Ag(NH_2–C_6H_4–OC_6H_{13})_2]^+$. (c) $[Ag(NH_2–CH_2–C_6H_4–OC_6H_{13})_2]^+$. (d) $[Ag(NH_2–C_6H_{13})_2]^+$.

The central graphic in Fig. 5 plots the values of L_{calc} and $d_{(001)}$ in the solid for the $n = 6$ member of the four series. The bis-*n*-hexylamine silver complex, known to be U-shaped, is taken for reference. Taking these plots and the expressions of $d_{(001)} = f(2n)$ calculated in Table 2, two different trends are suggested. The complexes derived from anilines (series **1** and **2**) show d-spacings close to but larger than their corresponding cationic lengths in the extended conformation, with l/CH_2 values clearly shorter than 1.26 Å. On the contrary, in benzylamine derivatives the spacing is shorter than the calculated length for the cation in the cisoid conformation (even shorter than the transoid conformation), and l/CH_2 is closer to 1.26 Å (1.20 Å for series **3** and 1.10 Å for series **4**). This behavior is similar to that reported for alkylamine silver complexes [7].

These results in the solid phase are compatible with a cationic arrangement for series **1** and **2** close to that shown in a bilayer arrangement of the cations with the amine ligands extended in opposite sense in a centrosymmetric conformation and the silver atoms in a plane. The interplanar distance should be almost the same as the cation length. A lamellar like mesophase is closely related to this solid structure.

For the benzylamine complexes the graphic in Fig. 5 reveals a behavior similar to the *n*-alkylamine complexes, and also that $d_{(001)}$ is dependent on the anion size (the

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[3] $l/CH_2 = d_{C–C}\text{sen}55°$; $d_{C–C} = 1.54$ Å.

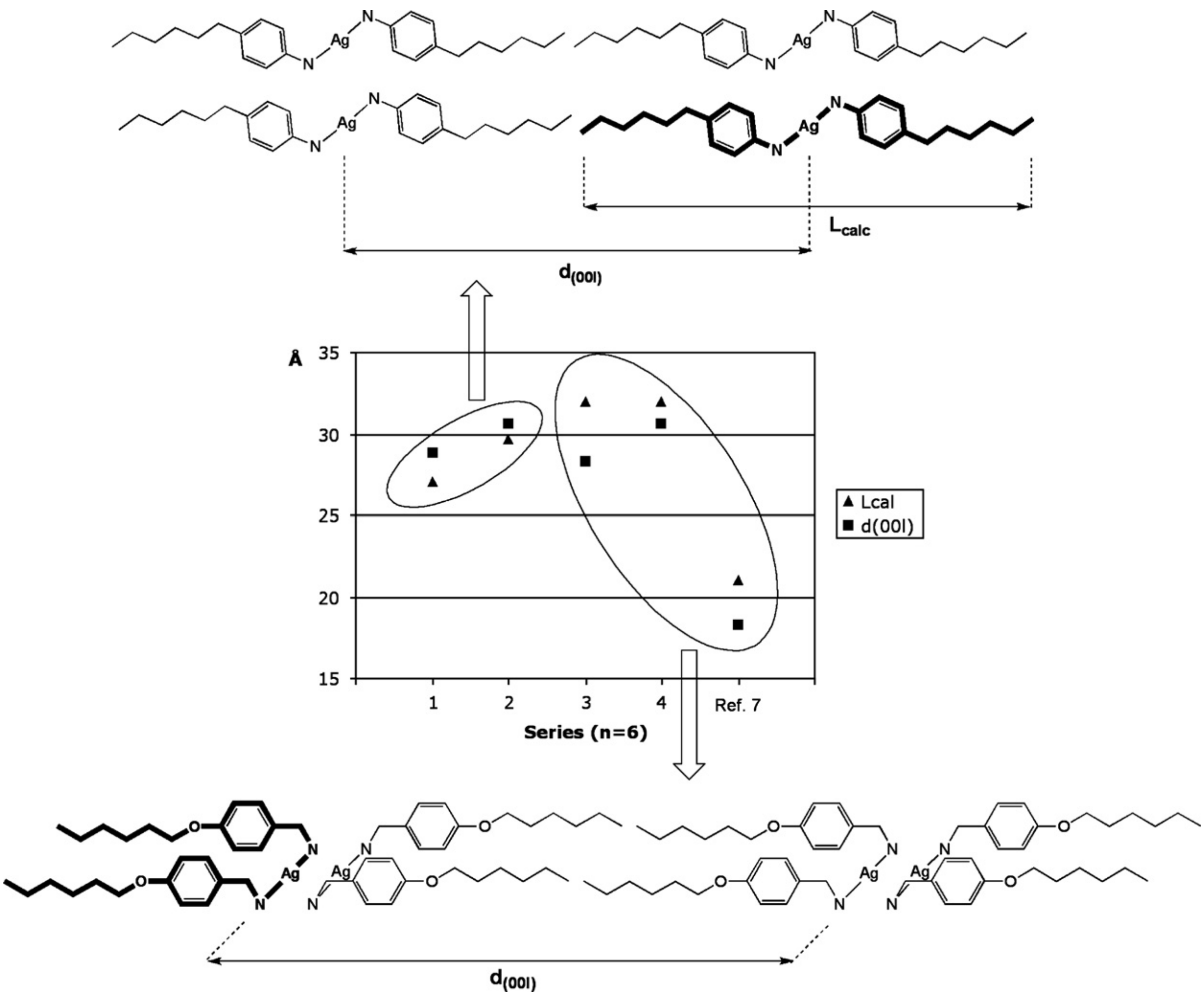

Fig. 5. Center: Plot of L_{calc} and $d_{(001)}$ values (solid state) for all the $n = 6$ members of the four series. The bis-n-hexylamine silver complex (Ref. [7]) is included for comparison. Up and down, proposed arrangement in solid state for series **1** and **2** (up) and **3** and **4** (down).

spacing increases for the bigger anion). This is consistent with a U-shaped cation conformation (as observed for the n-alkylamine complexes), not with the cation conformation calculated in gas phase (Fig. 4c or its transoid conformer), for which the d-spacing is not expected to be affected by the anion size. The values of l/CH_2 indicate a parallel orientation of the chains respect to the line defining L_{calc}, shorter for the tetrafluoroborate series due to the occurrence of chain interdigitation. The diffraction diagrams show a lamellar cation distribution. These data suggest an arrangement of the U-shaped benzylamine cations of the type shown in with the anions located in the space between contiguous silver atoms. Our results support that the complexes of series **3** and **4** behave as amphiphiles already in the solid state, where the preexistent separation of microphases will be the driving force for the mesophase formation upon melting.

Table 3
X-ray diffraction data for selected silver complexes in the solid and in the S_A mesophase

Compound	Solid	Mesophase		
	$d_{(001)}$ (Å)	$d_{(001)}$ (Å)	T (°C)	$\Delta d_{(001)}$ (Å)
1.8	32.70	29.44	100	3.26
1.10	36.76	31.30	105	5.46
3.8	32.77	30.48	90	2.29
3.10	37.42	32.70	100	4.72
4.8	34.21	29.35	80	4.86
4.10	39.49	31.60	90	7.89
$[Ag(NH_2–C_6H_{13})_2]NO_3$	18.28	18.45	40	−0.17
$[Ag(NH_2–C_8H_{17})_2]NO_3$	23.75	22.80	56	0.95
$[Ag(NH_2–C_{10}H_{21})_2]NO_3$	27.20	27.00	50	0.20
$AgSC_6H_{13}$	20.00	17.80	130	2.20

Additional information from variable temperature X-ray diffraction is given in Table 3. The diffraction experiments were carried out on selected samples of series **1**, **3** and **4** ($n = 8$, 10), excluding series **2** because of the marked decomposition it suffers just after melting, for some nitrate n-alkylamine compounds of reference 7 ($n = 6$, 8, 10), and for the reference compound $AgSC_6H_{13}$ [16a]. For each sample data were collected 10 °C above its melting point.

There is a striking difference $\Delta d_{(001)} = d_{(001)solid} - d_{(001)mesophase}$ for series **1**, **3**, and **4**, which is four to six times bigger than the same difference in the nitrate n-alkylamine silver complexes. This is not due to the high mesophase temperatures, which could deform in more extension the chains since $AgSC_6H_{13}$, also with a bilayered arrangement and a higher mesophase temperature shows a smaller difference in the layer spacing. We assign this great shortening in the layer spacing to interdigitation of the chains arising from the presence of the aromatic ring preventing a more compact space filling of the chains (the size of S in $AgSC_6H_{13}$ would produce the same effect to a smaller extent). The interdigitation will additionally help to promote the cylindrical symmetry and the uniaxiality of the lamellar assemblies required for the homeotropic textures experimentally observed.

4. Conclusion

The S_A mesophases produced by the bis-aniline and bis-benzylamine silver complexes studied derive directly from the solid molecular packing. The package of the alkylaniline and alkoxyaniline derivatives results in a bilayered structure where the cation has an extended centrosymmetric conformation. For the benzylamine derivatives, the structure in the solid and in the mesophase contains U-shaped cations which allows microsegregation of the organic part of the molecule from the inorganic Ag···(anion) part, giving rise to a bilayered structure where the cohesive forces are enhanced respect to any alternative extended configuration of the cations. Some degree of interdigitation of the terminal chains is observed for all the complexes with aryl containing ligands.

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