

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

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Abstract

Complexes $[\text{Ag}(\text{NH}_2\text{R})_2]\text{X}$, ($\text{X} = \text{NO}_3$, $\text{R} = -\text{C}_6\text{H}_4-\text{C}_n\text{H}_{2n+1}-p$, $-\text{C}_6\text{H}_4-\text{O}-\text{C}_n\text{H}_{2n+1}-p$, $-\text{CH}_2-\text{C}_6\text{H}_4-\text{O}-\text{C}_n\text{H}_{2n+1}-p$, $n = 6, 8, 10, 12, 14$; $\text{X} = \text{BF}_4$, $\text{R} = -\text{CH}_2-\text{C}_6\text{H}_4-\text{O}-\text{C}_n\text{H}_{2n+1}-p$, $n = 6, 8, 10, 12, 14$; $\text{X} = \text{OAc}$, $\text{R} = -\text{CH}_2-\text{C}_6\text{H}_4-\text{O}-\text{C}_{10}\text{H}_{21}-p$; $\text{X} = \text{CF}_3\text{SO}_3$, $\text{R} = -\text{CH}_2-\text{C}_6\text{H}_4-\text{O}-\text{C}_{10}\text{H}_{21}-p$) 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 $\text{Ag} \cdots (\text{anion})$ part. Some degree of interdigitation of the terminal chains is observed for all the complexes with aryl containing ligands.

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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, $[\text{Ag}(\text{NH}_2-\text{C}_n\text{H}_{2n+1}-n)_2]\text{X}$, ($\text{X} = \text{NO}_3$, BF_4 , OAc) that are very much related to this paper [7]. The compounds displayed a thermotropic lamellar mesophase corresponding to a bilayered arrangement of U-shaped $[\text{Ag}(\text{NH}_2-\text{C}_n\text{H}_{2n+1}-n)_2]^+$ 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: $[\text{Ag}(\text{NH}_2-\text{C}_6\text{H}_4-\text{C}_n\text{H}_{2n+1}-p)_2](\text{NO}_3)$
 $n = 6, 8, 10, 12, 14$

Series 2: $[\text{Ag}(\text{NH}_2-\text{C}_6\text{H}_4-\text{O}-\text{C}_n\text{H}_{2n+1}-p)_2](\text{NO}_3)$
 $n = 6, 8, 10, 12, 14$

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Series 3: $[\text{Ag}(\text{NH}_2\text{-CH}_2\text{-C}_6\text{H}_4\text{-O-C}_n\text{H}_{2n+1}\text{-p})_2](\text{NO}_3)$
 $n = 6, 8, 10, 12, 14$

Series 4: $[\text{Ag}(\text{NH}_2\text{-CH}_2\text{-C}_6\text{H}_4\text{-O-C}_n\text{H}_{2n+1}\text{-p})_2](\text{BF}_4)$
 $n = 6, 8, 10, 12, 14$

Compound 5: $[\text{Ag}(\text{NH}_2\text{-CH}_2\text{-C}_6\text{H}_4\text{-O-C}_{10}\text{H}_{21}\text{-p})_2](\text{OAc})$

Compound 6: $[\text{Ag}(\text{NH}_2\text{-CH}_2\text{-C}_6\text{H}_4\text{-O-C}_{10}\text{H}_{21}\text{-p})_2]$
 (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 K α radiation ($\lambda = 1.54 \text{ \AA}$). The samples were held on a rectangular $20 \times 15 \text{ mm}$ aluminium sample holder. The X-ray scanned from 3° to $70^\circ 2\theta$. XRD measurements in the mesophase were carried out with a Philips X'Pert PRO MPD X-ray diffractometer in θ - θ configuration equipped with a PW3373 generator and a high temperature chamber (Anton Paar HTK1200). Monochromatic Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) 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 $50^\circ 2\theta$. 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 $\text{H}_{2n+1}\text{C}_n\text{O-C}_6\text{H}_4\text{-CH}_2\text{NH}_2$ ($n = 6\text{--}14$)

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 $1/2 \text{ h}$. 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 $4 \times 15 \text{ mL}$ 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 ($4 \times 15 \text{ mL}$). 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 $\text{CHCl}_3/\text{EtOH}$ ($10:1$) as eluent. Yield: $65\text{--}70\%$. 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} ($\text{KBr}/\text{cm}^{-1}$): 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, $-\text{O-CH}_2-$) 3.79 (2H, s, $-\text{Ph-CH}_2-$); 1.51 (2H, br s $-\text{NH}_2$) 1.81–0.86 (m, alkyl chain).

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

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: $52\text{--}87\%$. 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} ($\text{KBr}/\text{cm}^{-1}$): 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, $-\text{NH}_2$); 2.43 (4H, t, J 7.7, $-\text{Ph-CH}_2-$) 1.51–0.89 (m, alkyl chain).

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