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Synthesis and study of novel azopyridine-containing hexacatenar silver mesogens

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Azopyridine-containing hexacatenar silver complexes have been synthesized and their liquid crystalline and photoisomerization behaviours investigated. These silver complexes (**1a–d**) exhibit hexagonal columnar liquid crystalline phases, whose structures were confirmed using polarizing optical microscopy and small angle X-ray diffraction.

1. Introduction

An emerging interest has been focused in recent years on the design of inherently photoactive liquid crystals (LCs), due to their potential applications in optical recording and display devices [1–3]. Research in this area has been directed towards the development of materials that can respond in a unique manner to the various properties of light such as wavelength, intensity and polarization [4–11]. Since metallomesogens are known to combine the physical characteristics of metal ions with the known properties of organic ligands, photo- and electro-chemically switchable metallomesogens can be designed by the proper choice of ligands [12–16]. Silver, platinum, and palladium complexes of substituted stilbazoles, as well as other pyridyl ligands, have been reported to form nematic, smectic, columnar and cubic phases [12, 17–20]. Although a number of photoactive LCs have been studied in recent years, very few reports exist on photoswitchable metallomesogens [13, 16, 21].

Polycatenar liquid crystals have been known since 1985 and this area has been extensively reviewed [22–25]. Various types of polycatenar metallomesogens, including silver(I)-containing hexacatenar complexes with alkylsulphate counter-ions, have also been reported in the literature [22, 26–28]. Long alkyl chain-containing counter-ions (such as dodecylsulphate) in the metallomesogens have been reported to reduce the transition temperatures [29]. Our interest in this area is concerned with the design and study of photoresponsive liquid crystals containing azopyridine moieties [16, 30–33]. In the present paper we report an investigation on the synthesis and studies of azopyridine-containing hexacatenar silver complexes (**1a–d**). The photophysical properties of these complexes are also described.

2. Experimental

2.1. *General*

Reagent grade reactants and solvents were used as received from suppliers. Extremely dry solvents were prepared by standard procedures [34]. Spectroscopic grade solvents were used for all measurements. Melting points are uncorrected and were recorded on a Mel-temp II melting point apparatus. Phase transitions were observed using a Nikon HFX 35A Optiphot-2 polarizing optical microscope, equipped with a Linkam THMS 600 heating and freezing stage connected to a Linkam TP92 temperature programmer. DSC scans were performed using a Du Pont DSC 2010 differential scanning calorimeter attached to a Thermal Analyst 2100 data station under air. The heating rate was $10^{\circ}\mathrm{C\,min^{-1}}$ in all cases. X-ray diffraction (XRD) studies were carried out using Cu K_α ($\lambda = 1.54$ Å) radiation from a rotating anode X-ray generator (Rigaku) and the diffraction pattern was collected on an image plate detector (Marresearch). IR spectra were recorded on a Perkin-Elmer Model 882 infrared spectrophotometer. The electronic spectra were recorded on a Shimadzu Model UV-3101 PC UV-Vis-NIR scanning spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 MHz FTNMR spectrometer using tetramethylsilane (TMS) as the internal standard. Steady state photolysis was carried out on an Oriel optical bench using a 200 W high pressure mercury lamp. Monochromatic light was obtained by using a 320 nm band pass filter.

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2.2. *Synthesis*

The first generation gallic acid derivatives required for the synthesis of the pyridine-based ligands were prepared using known procedures [35–38]. The silver complexes described in the present study (figure 1) were prepared by the stoichiometric reaction of silver dodecyl sulphate and the corresponding ligand in dry dichloromethane at ambient temperature in a vessel protected from light [16]. The complexes were characterized on the basis of elemental analysis and spectral data.

1a: yield 75%. IR $\nu_{\max}$ (KBr): 2952, 2919, 2866, 1725, 1586, 1500, 1467, 1427, 1381, 1334, 1228, 1202, 1109 cm^{-1}. UV $\lambda_{\max}$ (toluene): 320 nm ($\varepsilon = 4.6 \times 10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.9–1.0 (21H, m, CH_3), 1.2–1.8 (m, alkyl), 4.0 (12H, m, OCH_2), 4.1 (2H, t, CH_2OSO_3), 7.4 (8H, d, ArH), 7.9 (4H, d, ArH), 8.1 (4H, d, pyridyl H), 8.9 (4H, d, pyridyl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.76, 13.80, 14.05, 19.07, 19.20, 22.61, 25.79, 29.29, 29.37, 29.56, 29.60, 31.26, 31.84, 32.28, 68.52, 68.95, 73.20, 108.63, 117.49, 122.86, 123.16, 125.22, 143.36, 149.32, 149.85, 153.01, 154.94, 158.61, 164.45. Elemental analysis: calcd, C 61.22, H 7.06, N 5.95, S 2.27; found, C 61.72, H 7.44, N 6.27, S 2.62%.

1b: yield 86%. IR $\nu_{\max}$ (KBr): 2951, 2919, 2846, 1739, 1593, 1493, 1460, 1434, 1387, 1341, 1235, 1188, 1122 cm^{-1}. UV $\lambda_{\max}$ (toluene): 320 nm ($\varepsilon = 4.3 \times 10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.8 (21H, m, CH_3), 1.2–1.8 (m, alkyl), 4.0 (12H, m, OCH_2), 4.1 (2H, t, CH_2OSO_3), 7.3–7.4 (8H, d, ArH), 7.8 (4H, d, ArH), 8.0 (4H, d, pyridyl H), 8.9–9.0 (4H, d, pyridyl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.08, 22.66, 25.94, 26.08, 29.28, 29.36, 29.51, 29.63, 31.82, 31.89, 69.26, 73.59, 108.60, 117.50, 122.84, 123.21, 125.08, 143.36, 149.85, 152.98, 153.62, 154.94, 158.61, 164.45. Elemental analysis: calcd, C 66.01, H 8.48, N 4.81, S 1.83; found, C 65.88, H 8.7, N 5.16, S 2.12%.

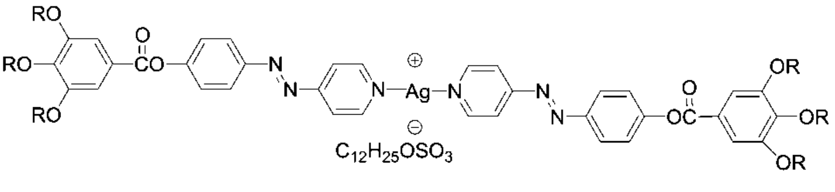
1c: yield 65%; IR $\nu_{\max}$ (KBr): 2919, 2853, 1732, 1586, 1500, 1474, 1427, 1374, 1334, 1228, 1195, 1135 cm^{-1}. UV $\lambda_{\max}$ (toluene): 320 nm ($\varepsilon = 5.0 \times 10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.8 (21H, m, CH_3), 1.2–1.8 (m, alkyl), 4.0 (12H, m, OCH_2), 4.1 (2H, t, CH_2OSO_3), 7.4 (4H, d, ArH), 7.5 (4H, d, ArH), 8.1 (4H, d, ArH), 8.2 (4H, d, pyridyl H), 9.0 (4H, d, pyridyl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.98, 22.65, 25.91, 26.28, 29.28, 29.38, 29.81, 29.63, 31.52, 31.69, 69.26, 73.59, 108.80, 117.43, 122.61, 123.42, 125.12, 143.65, 149.85, 152.98, 153.62, 154.84, 158.61, 165.45. Elemental analysis: calcd, C 69.10, H 9.42, N 4.03, S 1.53; found, C 68.89, H 9.66, N 5.50, S 1.81%.

1d: yield 70%. IR $\nu_{\max}$ (KBr): 2959, 2919, 2859, 1739, 1593, 1500, 1467, 1434, 1387, 1328, 1228, 1188, 1116 cm^{-1}. UV $\lambda_{\max}$ (toluene): 320 nm ($\varepsilon = 5.1 \times 10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.8 (39H, m, CH_3), 1.2–1.9 (m, alkyl), 3.9 (12H, m, OCH_2), 4.1 (2H, t, CH_2OSO_3), 7.4 (8H, d, ArH), 7.8 (4H, d, ArH), 8.0 (4H, d, pyridyl H), 8.9 (4H, d, pyridyl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.10, 11.15, 14.07, 14.11, 23.04, 23.09, 23.59, 23.78, 29.08, 29.22, 29.31, 29.60, 29.64, 30.37, 30.48, 31.87, 39.53, 40.61, 68.44, 71.31, 76.00, 108.00, 117.55, 122.86, 123.05, 125.12, 143.25, 149.77, 153.16, 153.64, 154.83, 157.64, 164.58.

3. Results and discussion

3.1. *Liquid crystalline properties*

The mesomorphic properties of the silver complexes (figure 1) were investigated using polarizing optical microscopy (POM), and the phase transition temperatures were confirmed by DSC as well as by small angle XRD. Optical microscopic studies were carried out to identify the mesophase of each of the compounds. The transitional behaviour of the complexes is listed in table 1. The silver complex **1a** ($R = C_4H_9$) melted at 101°C to form a mesophase and cleared at 111°C. When the mesophase was allowed to form at a very slow rate, a flower-like texture with Maltese crosses appeared suggesting the existence of a columnar



1a-d

a, $R = n\text{-}C_4H_9$
b, $R = n\text{-}C_8H_{17}$
c, $R = n\text{-}C_{12}H_{25}$
d, $R = n\text{-}CH_2CH(C_2H_5)(CH_2)_3CH_3$

Figure 1. Structure of the silver complexes.

Table 1. Phase transition temperatures and thermodynamic parameters of complexes **1a**–**d**. Cr = crystalline, Col = columnar, M = unidentified mesophase and I = isotropic phase.

Complex	Phase transition temperature/°C	$\Delta H_{\text{K-LC}}$/kJ mol^{-1} ($\Delta S_{\text{K-LC}}$/JK^{-1} mol^{-1})	$\Delta H_{\text{LC-I}}$/kJ mol^{-1} ($\Delta S_{\text{LC-I}}$/JK^{-1} mol^{-1})
1a	Cr 86 $\text{Cr}_1$101 Col 111 I	44.98 (120.4)	[a]
1b	Cr 79 M 92 Col 128 I	64.2 (182.5), 25.8 (70.8)	1.2 (3.0)
1c	Cr 83 Col 128 I	132.8 (373.0)	1.61 (4.0)
1d	Cr 88 Col 110 I	1.7 (4.6)	4.7 (12.4)

[a] Could not be detected due to small energy change.

mesophase [39]. A typical texture observed for **1a** is shown in figure 2. The DSC trace of **1a** showed two endothermic peaks during heating. The first transition attributed to a crystal to crystal change occurred at 86°C with a small associated enthalpy change of 7.6 kJ mol^{-1} ($\Delta S = 21.2$ J K^{-1} mol^{-1}). A crystal to mesophase transition was observed at 101°C with an enthalpy change of 45 kJ mol^{-1} ($\Delta S = 120.3$ J K^{-1} mol^{-1}). No peak attributable to an LC to isotropic phase transition was observed in DSC, possibly because the associated enthalpy change was very small. The complex cleared at 111°C, as observed under POM. Similar LC behaviour was observed for **1c**. However, the silver complex **1b** melts to an unidentified mesophase at 79°C before the formation of a columnar LC phase. This was confirmed by the DSC trace, which contains three endotherms. The first transition at 79°C can be attributed to a transition from crystal to the unidentified mesophase, and the second peak observed at 91.7°C is due to the formation of a columnar LC phase. The *rac*-2-ethylhexyl derivative, **1d** has low enthalpy and entropy changes compared with other members of this series, indicating lower ordering in its crystalline state.

The texture of the crystalline material on cooling, as observed under the microscope, was identical to that seen for the LC phase. A similar observation has been reported earlier for columnar liquid crystalline alkyl arene carboxylates [40]. Also, in all these complexes (**1a**–**d**) no crystallization peaks were observed in the DSC traces obtained on cooling. It should be noted that the material obtained on cooling was highly light scattering and not glassy. Small angle X-ray analysis of the silver complexes was used to confirm the existence of columnar hexagonal LC phases in these materials. The X-ray patterns consist of three sharp and intense reflections in the small angle region and two diffuse scattering halos in the wide angle region. The outer diffuse halo corresponds to liquid-like order of molten hydrocarbon chains, and the inner one has been assigned to periodicity along the column axis [41]. For example, the X-ray diffractogram of silver complex **1c** contains three peaks in the small angle region corresponding to the layer spacings $d = 41.62$, 24.06 and 15.71 Å. The ratio of the layer spacings is $1:\sqrt{3}:\sqrt{7}$ confirming the formation of a hexagonal lattice. A representative X-ray pattern of the columnar phase of **1c** at 105°C is shown in figure 3.

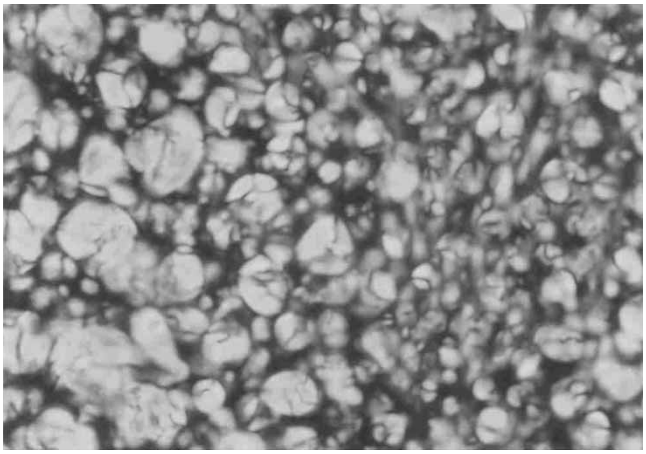


Figure 2. Optical photomicrograph showing columnar texture of **1a** formed at 93°C on cooling.

3.2. *Photoisomerization studies*

Photoirradiation of the silver complexes **1a**–**d** (in toluene) at a wavelength of 320 nm resulted in a decrease of the optical density of the π–π* electronic transitions of the azopyridyl chromophores and a small increase in the 450 nm region due to formation of the *cis*-isomer. A steady state was reached within 3 min of photoirradiation. The kinetics of the thermal process of *cis-trans*-isomerization for these silver complexes at room temperature was also investigated. Solutions were irradiated using a wavelength of 320 nm for 3 min, and the recovery of the optical density at the wavelength corresponding to the maximum of π–π* electronic transition was measured. The rate constants for thermal isomerization were obtained by fitting the experimental points to a first-order rate equation. It was found that the rate of the reverse *cis-trans*-isomerization of the silver complexes was ~50–100 times greater than that

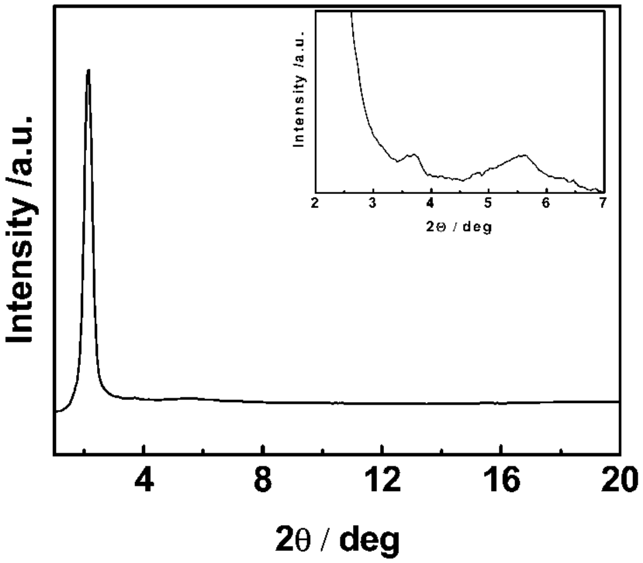


Figure 3. X-ray diffraction pattern of columnar phase of 1c at 105°C. Inset shows the expanded view of lower angle ($2\theta = 2$–7°).

of the ligands. This can be attributed to the complexation of the pyridyl group by Ag^+, which makes it more electron deficient, thereby enhancing the donor–acceptor nature of the azo moiety. 4,4′-Donor–acceptor-substituted azobenzenes are reported to undergo thermal isomerization at much faster rates than unsubstituted and monosubstituted azobenzene derivatives [42, 43]. Table 2 lists the estimated rate constants for the process of *cis*-*trans*-isomerization of the complexes and their ligands.

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Table 2. Comparison of rate of reverse *cis*-*trans*-isomerization of ligands and their silver complexes in toluene.

Complex	Rate × $10^3/s^{-1}$	Rate × $10^3/s^{-1a}$ (ligand)
1a	9.6	0.11
1b	4.1	0.08
1c	3.9	0.11
1d	4.4	0.04

[a] Rate of reverse *cis*-*trans*-isomerization of corresponding azopyridine ligands.

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