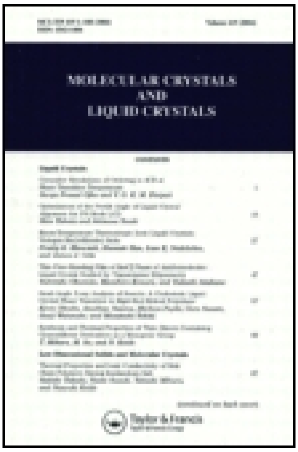

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Polymorphic Ionic Mesogens of Silver(l): Ionic Materials Exhibiting a Thermotropic Cubic Mesophase

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Polymorphic Ionic Mesogens of Silver(I): Ionic Materials Exhibiting a Thermotropic Cubic Mesophase

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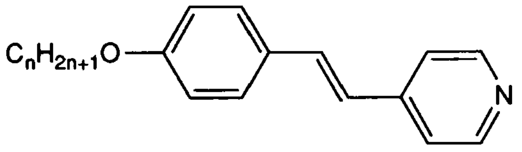
Reaction of *trans*-4-alkyloxy-4′-stilbazoles (*n*-OPhVPy) with silver dodecylsulphate (AgDOS) led to the complexes [Ag(*n*-OPhVPy)$_2$][DOS] which showed thermotropic mesomorphism. All homologues from methyloxy ($n = 1$) to dodecyloxy ($n = 12$) have been synthesised. The complexes showed a nematic phase at short chain lengths, but at longer chain lengths, smectic C and A phases were observed in addition to an isotropic mesophase (M$_I$), similar to the recently characterised D phase. The mesomorphism was determined using optical microscopy, DSC and X-ray scattering.

INTRODUCTION

Anhydrous, thermotropic, ionic liquid crystals have been known for some time and their mesomorphism has been extensively studied.[3] For many of these materials, the phase behaviour may be typified by considering the alkali metal salts of alkylcarboxylic acids, where on heating, the compound passes through a number of crystalline modifications before melting into the lamellar (or neat) mesophase and finally clearing to an isotropic state. While some ionic systems are known to show a richer mesomorphism,[4] most tend only to show a lamellar mesophase. Some other metal-containing systems have also been described,[5] namely the bis(alkylammonium) tetrahalometallates of zinc, iron and cadmium ([$C_nH_{2n+1}NH_3$)$_2$]

[MX_4]; M = Fe, Cd, X = Cl; M = Zn, X = Cl, Br), which are reported to show a lamellar mesophase. Also noteworthy is 4-cyano-*N*-hexadecylpyridinium iodide which has been reported[6] to show a partially ordered, interdigitated smectic B phase.

We have previously reported[7] the synthesis and phase behaviour of the *trans*-4-alkyloxy-4′-stilbazoles (**I**) (abbreviated to *n*-OPhVPy where *n* denotes the number of carbon atoms in the terminal alkyl chain) and of some of their mesomorphic metal complexes.[8] We now report a series of thermotropic ionic mesogens formed by complexing these stilbazoles to silver(I). Some of this work has already appeared in preliminary communications.[9]



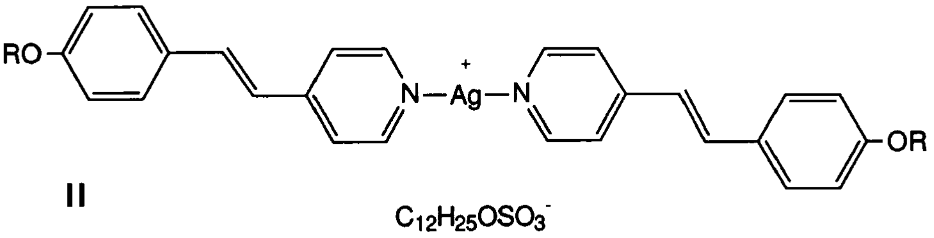
I

trans-4-alkyloxy-4′-stilbazole

RESULTS AND DISCUSSION

Synthesis and Characterisation

The proposed structure of the complexes under investigation is shown below:



The complexes can be prepared in one of two ways. In the first method, the stilbazole was reacted with $AgBF_4$ in acetone to give [Ag(*n*-OPhVPy)$_2$][BF_4], which was then reacted with sodium dodecylsulphate (NaDOS) in acetone to give [Ag(*n*-OPhVPy)$_2$][DOS] (**II**). A better route used anhydrous AgDOS (prepared from $AgNO_3$ and NaDOS) which was then reacted directly with two equivalents of the stilbazole in dichloromethane.

Attempts to characterise the complexes by single crystal X-ray diffraction were frustrated by X-ray sensitivity which caused the intensity of the reflections to drop almost to zero after two hours. Nevertheless, it has been possible to carry out some X-ray scattering experiments on the mesophase and these results are presented below. Very recently however, we have been able to obtain single crystals of [Ag(MeOPhVPy)$_2$][$C_8H_{17}OSO_3$] which have proved sufficiently stable to X-rays for a full data set to be collected.[10] The results of this structural investigation will be reported in due course.

Thermal Stability and Mesomorphism

The mesomorphism of complexes with the tetrafluoroborate anion was not extensively investigated due to high moisture sensitivity, very high transition temperatures and accompanying decomposition. In some freshly-prepared samples with longer alkyloxy chains, S_C and S_A phases were identified and this is consistent with work carried out on related complexes of 4′-alkyloxy-*N*-(4-pyridylbenzylidene)anilines and 4′-(4-alkyloxyphenyl)pyridine carboxylates with $AgBF_4$.[11]

In order to reduce the transition temperatures of these salts, the tetrafluoroborate anion was replaced with amphiphilic dodecylsulphate. This approach was successful and the typical clearing temperatures were reduced from about 300°C (BF_4) to around 170°C (DOS). In general, the thermal stability of the DOS salts was good and there was no evidence for decomposition for most samples on cooling from the mesophase. Stability to light (visible and uv) was also not a major problem, although as a precaution the complexes were stored in the dark.

The phase behaviour was studied using polarising optical microscopy, differential scanning calorimetry and X-ray scattering; full details of transition temperatures and thermodynamic data are presented in Table I and the phase diagram for the system is shown in Fig. 1.

The first three homologues in the series (**II**, $n = 1$–3) all showed only a nematic phase, despite the fact that two of the parent stilbazoles (**I**, $n = 1, 2$) were non-mesomorphic. To our knowledge, these materials (and directly related complexes),[9] represent the first examples of anhydrous ionic materials to show a thermotropic nematic phase. The nematic phase was identified on the basis of optical microscopy where the characteristic two- and four-brush isogyres confirmed the assignment, and also by X-ray scattering (see below). Attempts to identify the phase *via* a contact preparation with the nematic phase of 4-cyano-4″-pentyl-*p*-terphenyl (5CT) were frustrated by the appearance of an injected smectic A phase at the boundary between the two nematic phases.

That ionic complexes form a nematic phase is quite surprising when the anisotropic nature of the forces associated with the formation of a nematic phase is compared with the isotropic nature of ionic forces. It is however possible for these complexes that the cations and anions are associated as intimate ion pairs and thus anisotropic attractive and repulsive interactions overcome the isotropic coulombic forces; preliminary conductivity measurements made using the nematic phase of the methyloxy derivative would seem to support the concept of ion-pairing.

We had previously reported the butyloxy derivative as showing only a nematic phase,[9b] but exhaustive re-examination of the material led us to re-interpret our original observations.[9c] Thus the complex melted at 147°C to give a strongly homeotropic S_A phase which gave way to a similarly strongly homeotropic nematic phase at 166°C which cleared at 178°C. On cooling, the S_A range extended below the melting point to 144.5°C when a re-entrant nematic phase was observed and subsequently gave way to an S_C phase at 136.5°C.

The mesomorphism of the pentyloxy derivative on heating was the same as that of the butyloxy compound, showing an S_A phase followed by a nematic. The re-entrant nematic was not observed, although a monotropic S_C phase was found just below the melting point.

TABLE I

Transition temperatures for [Ag(n-OPhVPy)$_2$][DOS]

n	Transition	T/°C	ΔH/J g^{-1}	ΔS_m/R
1	K-N	129	39.6	9.4
	N-I	162	5.3	1.2
2	K-N	135	25.4	6.2
	N-I	177	0.7	0.2
3	K-N	144	28.1	6.9
	N-I	164	0.8	0.2
4	K-S$_A$	149	32.7	8.1
	S$_A$-N	165	0.7	0.6
	N-I	178	0.2	0.1
	(S$_A$-N$_r$)	144.5		
	(N$_r$-S$_C$)	136.5		
5	K-S$_A$	144		
	S$_A$-N	157	27.7	7.2
	N-I	176	0.3	0.1
	(S$_A$-S$_C$)	143		
6	K-M$_I$	138	25.1	6.8
	M$_I$-S$_A$	156	2.3	0.6
	S$_A$-I	185	1.2	0.2
	S$_A$-S$_4$	143		
7	K-S$_C$	132	27.3	8.0
	S$_C$-S$_4$	135		
	S$_C$-M$_I$	139	1.2	0.4
	M$_I$-S$_A$	152	1.8	0.3
	S$_A$-I	179	1.1	0.3
	(S$_A$-S$_C$)	138		
8	K-S$_C$	135		
	S$_C$-M$_I$	139	25.7	7.4
	M$_I$-S$_A$	153	1.9	0.5
	S$_A$-I	178	1.3	0.3
	(M$_I$-S$_4$)	137		
9	K-S$_C$	133	29.7	9.0
	S$_C$-M$_I$	139	3.0	0.9
	M$_I$-S$_A$	153		
	S$_A$-I	180	1.4	0.4
10	K-S$_C$	123	30.0	9.1
	S$_C$-M$_I$	135	3.5	1.0
	S$_C$-S$_4$	133		
	M$_I$-S$_A$	158		
	S$_A$-I	171	1.2	0.3
11	K-S$_C$	116	31.5	9.8
	S$_C$-M$_I$	135	2.5	0.8
	M$_I$-S$_A$	156	1.9	0.6
	S$_A$-I	180	decomp	
	S$_4$-M$_I$	147		
	S$_4$-S$_C$	121		
12	K-S$_C$	108	25.9	9.0
	S$_C$-M$_I$	123	3.8	1.2
	M$_I$-S$_A$	153	2.4	0.8
	S$_A$-I	168	0.5	0.2
	S$_4$-S$_C$	113		
	M$_I$-S$_C$	122		
	S$_4$-M$_I$	136		

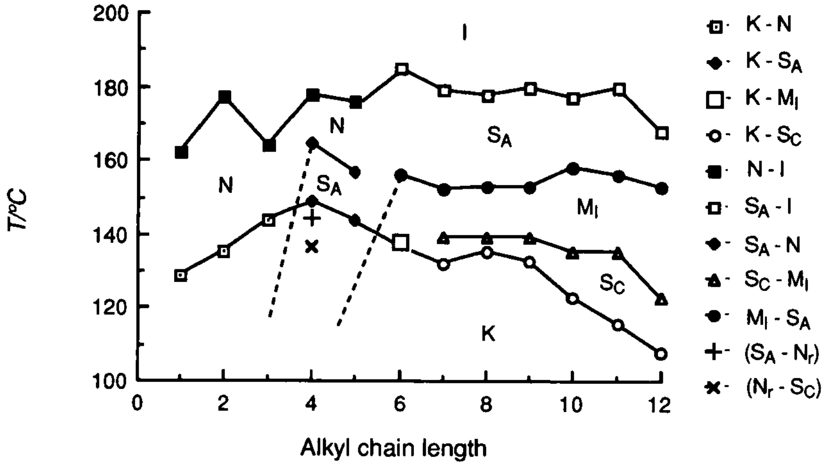


FIGURE 1 Phase diagram for [Ag(*n*-OPhVPy)$_2$][DOS].

With one exception, all of the higher homologues showed the same mesomorphic sequence and will therefore be described together. Examination of the phase diagram shows that for the lower homologues, the commonly-found alternation in clearing temperature is observed, but this disappears where the uppermost phase is S_A. While this is not expected, it may lend support to the assignment of the S_A phase as strongly interdigitated (see below). The phase diagram also shows that the thermal stabilities of all the phases decrease in the dodecyloxy homologue. While the origin of this effect is unclear, it cannot be assigned to low purity of the materials as both microanalysis (Table III) and ^{1}H nmr show the complex to be of good purity.

For the heptyloxy-dodecyloxy homologues, the crystals melted to form an S_C phase which then underwent a transition to a viscous, optically isotropic mesophase (designated M_I) which grew in as square edges through the schlieren texture of the S_C phase (Fig. 2). This phase persisted until transition to a strongly homeotropic S_A phase which eventually cleared. The phase behaviour of the hexyloxy derivative differed only in that the crystal melted straight into the M_I phase and no S_C phase (enantiotropic or monotropic) was seen. The S_A and S_C phases of these materials were characterised by a combination of optical microscopy, contact preparations and X-ray scattering. Although the S_A phase was strongly homeotropic, it was possible to observe characteristic focal-conic fan structures around defects in the preparation and the textures formed on application of light pressure to the coverslip. The optical texture of the S_C was also characteristic, but in this case the assignment was confirmed by a contact preparation with the S_C phase of 4-dodecyloxybenzoic acid at 110°C. Assignment as S_A and S_C for these phases was supported by X-ray studies (see below). It is of interest to note that both the S_A phase and the nematic phase showed a strong tendency for homeotropic alignment; similar observations were made by Serrano and co-workers with related systems.[11] Transitions from S_A to N were therefore identified by passing slowly through the transition and watching for the onset of the flashing characteristic of the nematic phase. Transition temperatures obtained in this way agreed well with those found by DSC.

FIGURE 2 Photomicrograph of S_C–M_I transition at 141.5°C on heating [Ag(8-OPhVPy)][DOS]. See Color Plate III.

The appearance of the M_I phase was of great interest and its properties were very reminiscent of the (smectic) D phase of the laterally substituted biphenylcarboxylic acids[12] (Fig. 3).

Thus the phase appeared above an S_C phase (except in the hexyloxy derivative) and below a strongly homeotropic S_A phase (this would distinguish it from other isotropic mesophases which appear below the S_C phase).[13] The phase grew in very slowly from either phase and appeared as isotropic areas behind square fronts; its viscosity was very much higher than either of the two mesophases which formed

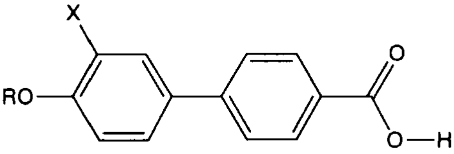


FIGURE 3 Structure of the biphenylcarboxylic acids showing the D phase (R = $C_{16}H_{33}$ or $C_{18}H_{37}$; X = CN or NO_2).

its boundary. Transitions from S_A to M_I were readily identified by the appearance of square-edged features, despite the strongly homeotropic nature of the S_A phase. In addition, another phase was often observed with the M_I phase and its behaviour appeared identical to that reported for the S_4 phase which is associated with the D phase. This phase appeared as highly birefringent lancets (the textural resemblance of this phase to the discotic phase of di(isobutyl)silanediol[14] led some authors to speculate on its structure)[15] which in general appeared on cooling the S_A phase and which on further cooling coalesced to give a mosaic texture, although on several occasions (unfortunately without any pattern) it was observed to appear on heating the S_C, either on the first or subsequent heating runs. In common with the S_4 phase, this phase could be seen to undergo transition to M_I, S_A and S_C, although the conditions for these transitions were not well-defined. Thus, the temperatures quoted for transitions involving this mesophase (designated S_4) are the temperatures at which the transitions were observed to occur and are not necessarily the true transition temperatures in all cases (because of supercooling). Indeed, it has been suggested that transitions to the S_4 phase are kinetic rather than thermodynamic.[16] Because of the uncertainty associated with the appearance of this S_4 phase, it has not yet been possible to investigate its structure using X-ray techniques, although the much greater range and stability of the phase in these materials should mean that such structural investigations will be possible.

We should comment here on the discrepancy between the mesomorphism reported here for $[Ag(8\text{-OPhVPy})_2][DOS]$ and that reported by us in an earlier publication.[9a] Previously, we reported this complex to show a smectic B and a smectic A phase (K 144 S_B 164 S_A 177 I), whereas now we find S_C and M_I in addition to S_A, but no S_B. Nevertheless, the published mosaic texture was consistent with a fluid phase assigned as S_B. The materials in the previous publication were prepared by metathesis of the BF_4 salt with NaDOS, a reaction which we now know to be generally less reliable than the direct reaction of *n*-OPhVPy with AgDOS. NaDOS cannot be completely dehydrated and always retains 1/12 mole of water, which does not easily show up by standard analytical techniques (nmr, ir, microanalysis). We can conclude that the material studied and reported previously retained some of this water in the crystal lattice and that this resulted in a change in phase behaviour. However, treatment of an anhydrous sample of the complex with aqueous acetone does not affect the phase behaviour, implying that water needs to be retained at the time of preparation in order to modify the mesomorphism in these systems.

It is interesting to note certain structural similarities which exist between the silver complexes and the biphenylcarboxylic acids (**III**, Fig. 4). The biphenylcarboxylic acids (**III**) have long alkyloxy chains ($C_{16}H_{33}O$—, $C_{18}H_{37}O$—), a lateral

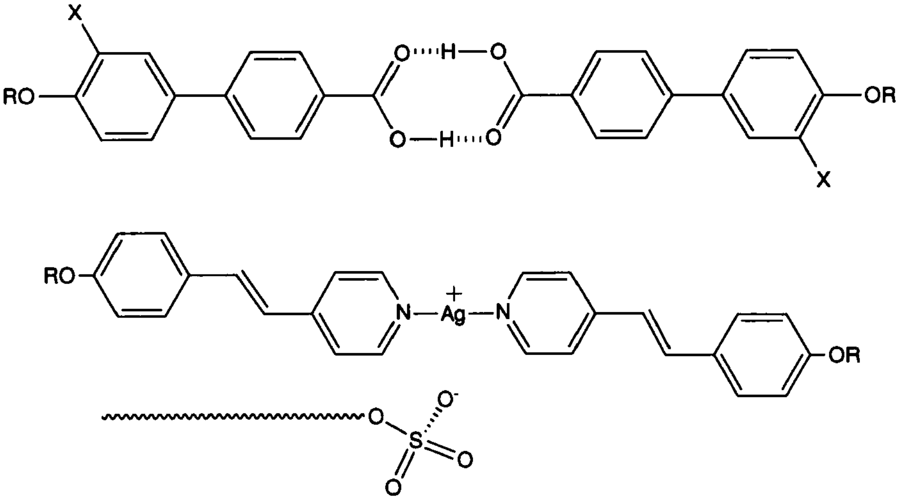


FIGURE 4 Structural comparison between the silver complexes and the biphenylcarboxylic acids.

polar substituent (NO_2, CN) and exist as hydrogen-bonded dimers in the mesophase. The silver salts also have a 'dimeric' arrangement of two mesogenic ligands held together by a central cation and the cation/anion association may be regarded as having a lateral polar function. In contrast to the biphenylcarboxylic acids, the silver complexes show the M_I phase at much shorter alkyl chain lengths.

X-ray Studies

$[Ag(9\text{-}OPhVPy)_2][DOS]$. Preliminary studies were carried out using a simple flat plate diffraction apparatus mounted on a sealed tube source. However, this required the sample to be exposed to high temperatures (>150°C) for several hours. At such high temperatures and in the presence of an X-ray beam, there was a danger of decomposition and hence slight changes in the layer spacing could not be confidently assigned to phase changes. For this reason it was decided to investigate the structure using the X-ray diffraction and differential scanning calorimetry (XDDSC) technique developed at Bristol.[17] Thus, the DSC (on heating) was recorded while the sample was simultaneously subjected to synchrotron X-radiation and the scattering was measured. The sample was heated at a rate of 5°C min^{-1} from 90° to 175°C. X-ray patterns were recorded using a linear position-sensitive detector at 1° intervals. The observed intensities are shown in Fig. 5 as a function of scattering vector and temperature. However, for the sake of clarity and also to improve the statistics, we have averaged each spectrum in Fig. 5 over 2°C. The spectra in Fig. 6 give a close-up view of the layer peaks.

On heating, the sample in its crystalline state melted at 133°C. Three reflections are observed for the mesophase (133–139°C). The reflections at 34.7 Å and 17.2 Å were sharp while the reflection observed at 4.6 Å was diffuse. This identified the phase as lamellar with no in-plane long-range order. The calculated length of the molecule (from CPK models) was 50.3 Å and by using the 001 reflection (34.7 Å) as the layer spacing, a tilt angle (θ_t) of 46° was calculated (from $\theta_t = \cos^{-1}$

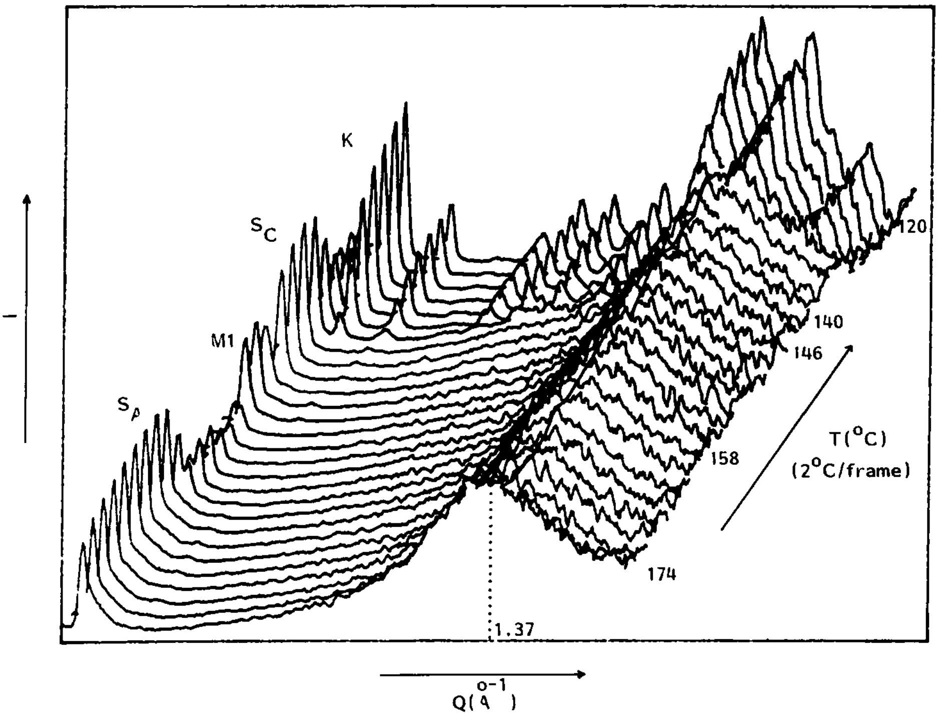


FIGURE 5 X-ray diffraction scan from $[Ag(9\text{-}OPhVPy)_2][DOS]$ on heating from 120° to 175°C by XDDSC technique. The intensity (I) has been corrected for Lorenz and polarisation factors. The horizontal scale is scattering vector (Q) and the corresponding *d* spacings are given in the text.

(*d*/*l*)). However, some interdigitation of the layers can be expected, so θ_t might be less than 46°. This was consistent with an S_C phase as suggested by the optical studies.

The M_I phase showed up between 146° and 157°C and reflections were observed at 38.1 Å, 33.2 Å and 4.6 Å. The structure was certainly not lamellar in nature and indexing the first two reflections as 111 and 200, respectively, suggested the possibility of a FCC lattice with a lattice parameter of 66 Å. This would identify the mesophase as cubic and is not inconsistent with the D phase (see above). However, unequivocal phase identification will require X-ray studies on monodomain samples. While the DSC and optical microscopy did not show any phase between the lamellar S_C phase and the M_I phase, the X-ray data from XDDSC did show a new pattern between 139° and 145°C. No endotherm accompanied the transition from this phase to the M_I phase in the accompanying DSC trace. While it was possible to deduce that the phase was lamellar, no other conclusions could be drawn in the absence of optical observations. However, it is possible that the 'phase' is associated with the reorganization of the molecules during the transition from the S_C phase to the cubic M_I phase which was observed to be slow.

The phase observed between 158° and 174°C gave reflections at 39.5 Å, 20.0 Å (sharp) and 4.6 Å (diffuse). This identified the phase as lamellar with no inplane long-range order. This was consistent with an S_A phase as suggested by optical

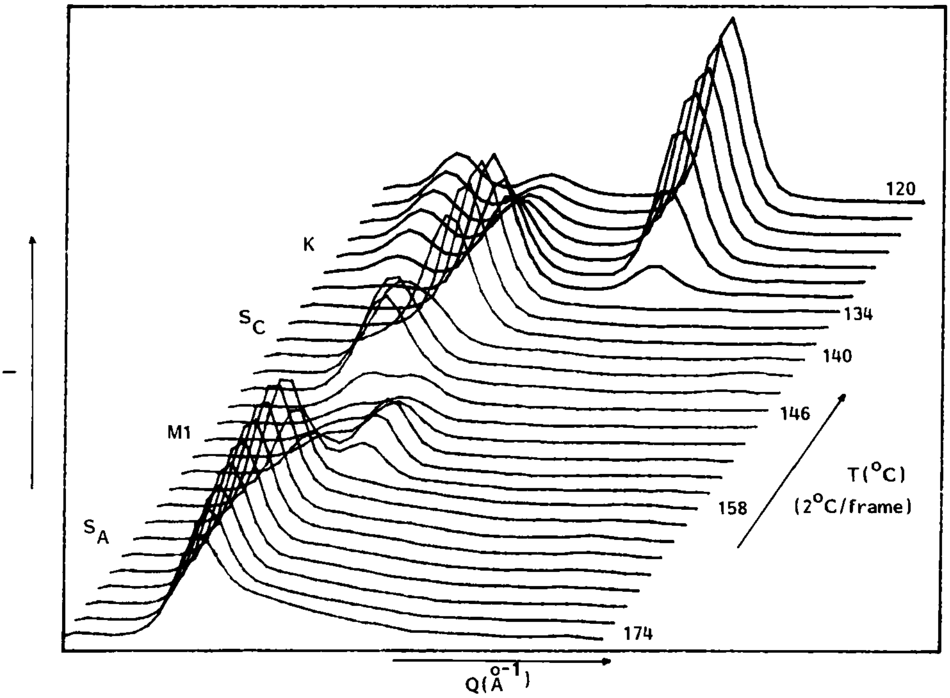


FIGURE 6 An expanded view of the 'layer peaks' of Figure 5.

studies. The layer spacing of 39.5 Å was considerably shorter than the calculated length (50.3 Å) and suggested an S_A phase with a large random tilt and/or interdigitation of the layers.

[Ag(3-OPhVPy)$_2$][DOS] and [Ag(12-OPhVPy)$_2$][DOS]. These two complexes were investigated using the Daresbury synchrotron radiation source on beam line 8.2 and the data were collected on film.

For [Ag(3-OPhVPy)$_2$][DOS], the X-ray data were collected at 150°C for the nematic phase from a sample which had been aligned in a magnetic field. The principal long spacing was found to be 33.1 Å, which matched well with the molecular length of 35.1 Å as measured using CPK models. The position of the diffraction pattern showed that the material had a positive diamagnetic anisotropy.

For [Ag(12-OPhVPy)$_2$][DOS], (molecular length 55.4 Å by CPK models) the X-ray data were collected at 138°C for the M_I phase and at 161°C for the S_A phase. At 138°C, reflections were observed at 43.6, 36.7, 26.0, 22.1, 21.2 and 20.4 Å. Indexation of these lines using the program developed by Paszkowic[18] showed them to be (111), (200), (220), (311), (222) and (320) respectively and gave a lattice parameter of 73.4 Å with an error factor of 0.03. This would suggest a cubic lattice in common with the nonyloxy homologue but the presence of a (320) reflection rules out a face-centered system. At 161°C, reflections at 43.6 Å (sharp) and 4.7 Å (diffuse) were found and again, comparison of this spacing with the measured molecular length would imply extensive interdigitation and/or large random tilt. Further support for the idea that the S_A phase is interdigitated comes from the observation that the odd-even effect disappears for the materials with S_A as the highest temperature phase, so that the effect of the terminal carbons on the anisometry of the complexes is greatly reduced.

$[Ag(9\text{-}OPhVPy)_2][DOS]$ was also studied at Daresbury in this way and the results are totally consistent with those obtained by XDDSC.

EXPERIMENTAL

Acetone was distilled from calcium sulphate and dichloromethane was neutralized with potassium carbonate prior to use. Elemental analyses were determined by the University of Sheffield Microanalysis Service and NMR spectra were recorded on a Bruker AM250 spectrometer. Analysis by DSC was carried out on a Perkin-Elmer DSC7 instrument using heating rates of 10 K min^{-1}. Analysis by hot-stage optical microscopy was carried out using a Zeiss Labpol microscope equipped with a Link-Am TH600 hot-stage and PR600 controller.

4-Alkyloxy-4′-stilbazoles were prepared as previously described[7] and silver tetrafluoroborate (Fluorochem) was used as supplied. Silver dodecylsulphate was prepared by mixing aqueous solutions containing sodium dodecylsulphate and a slight excess of silver nitrate, filtering and washing the precipitate and drying under vacuum for several days.

The tetrafluoroborate salts were prepared as described in the example below and the analytical results are included for completeness (Table II).

Bis(4-dodecyloxystilbazole)silver(I) tetrafluoroborate

A solution of 4-dodecyloxystilbazole (1.00 g, 2.74 mmol) in dry acetone (10 cm^3) was added to a stirred solution of silver tetrafluoroborate (267 mg, 1.34 mmol) in the same solvent (5 cm^3); stirring was continued (2h/ambient) with the vessel protected from light. The resulting pale yellow precipitate was filtered, washed with dry acetone (3 × 5 cm^3) and dried under vacuum.

TABLE II

Microanalytical data for $[Ag(n\text{-}OPhVPy)_2][BF_4]$

n	Yield (%)	Microanalysis: Calculated (Found)		
		C	H	N
1	96	54.5(54.8)	4.2(4.3)	4.5(4.5)
2	85	55.8(55.8)	4.7(4.5)	4.3(4.1)
3	90	57.1(57.1)	5.1(4.9)	4.2(4.0)
4	86	58.2(58.2)	5.5(5.5)	4.0(3.9)
5	89	59.3(59.1)	5.8(5.7)	3.8(3.6)
6	87	60.3(60.0)	6.1(6.2)	3.7(4.0)
7	94	61.2(61.1)	6.4(6.4)	3.6(3.5)
8	98	62.0(61.9)	6.7(6.7)	3.4(3.4)
9	95	62.8(62.8)	6.9(7.1)	3.3(3.3)
10	90	63.5(63.5)	7.2(7.3)	3.2(3.2)
11	91	64.3(64.1)	7.4(7.5)	3.1(3.1)
12	91	64.9(64.7)	7.6(7.6)	3.0(2.9)

Bis(4-undecyloxystilbazole)silver(I) dodecylsulphate-From the BF_4 Salt

This method is included again for completeness; the direct reaction of the stilbazole with AgDOS is generally to be preferred and all of the data quoted in this paper refer to complexes prepared by direct reaction.

A solution of sodium dodecylsulphate (132 mg, 0.45 mmol) in dry acetone (10 cm^3) was added to a stirred solution of the tetrafluoroborate complex (274 mg, 0.3 mmol) in the same solvent (5 cm^3); stirring was continued (2h/ambient) with the vessel protected from light. The acetone was removed under reduced pressure and the residue extracted with dichloromethane (3 × 5 cm^3). The solution was filtered to remove excess of sodium dodecylsulphate and the dichloromethane was removed from the filtrate under reduced pressure to yield the product as a pale yellow powder which was dried under vacuum. Yield = 279 mg (86%). Microanalysis: Calculated for $C_{60}H_{91}AgN_2O_6S$: C 67.0 (66.9), H 8.5 (8.7), N 2.6 (2.7), S 3.0 (3.1)

Bis(4-octyloxystilbazole)silver(I) dodecylsulphate-Direct Reaction

A solution of 4-octyloxystilbazole (338 mg, 1.08 mmol) in dichloromethane (10 cm^3) was added to a stirred suspension of silver dodecylsulphate (201 mg, 0.54 mmol) in the same solvent (10 cm^3) and stirring continued (5 mins/ambient) with the vessel protected from light. The solvent was removed under reduced pressure, the residue was crystallised from hot acetone and the product filtered off as a pale yellow solid. Microanalytical data for these complexes are collected in Table III.

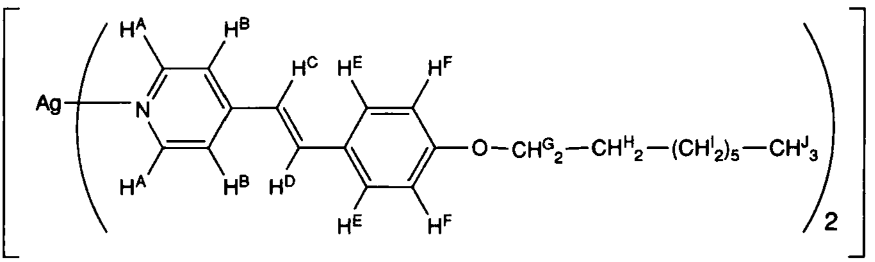
TABLE III

Microanalytical data for $[Ag(n\text{-OPhVPy})_2][C_{12}H_{25}OSO_3]$

		Microanalysis: Calculated (Found)			
n	Yield	C	H	N	S
1	70	60.4(60.3)	6.5(6.3)	3.5(3.2)	4.0(4.5)
2	77	61.2(60.6)	6.7(6.4)	3.4(3.2)	3.9(4.2)
3	75	62.0(61.3)	7.0(6.6)	3.3(3.0)	3.8(3.9)
4	72	62.8(62.8)	7.2(7.0)	3.2(3.0)	3.6(4.0)
5	79	63.5(63.5)	7.4(7.6)	3.1(3.0)	3.5(3.8)
6	70	64.2(63.9)	7.6(7.0)	3.0(3.0)	3.4(3.6)
7	58	64.8(64.8)	7.8(7.9)	2.9(2.7)	3.3(3.8)
8	74	65.4(65.2)	8.0(7.5)	2.8(2.7)	3.2(3.6)
9	71	65.9(65.7)	8.2(8.1)	2.7(2.9)	3.1(3.5)
10	87	66.5(66.8)	8.4(8.5)	2.7(2.6)	3.1(3.3)
11	86	67.0(66.9)	8.5(8.7)	2.6(2.7)	3.0(3.1)
12	84	67.4(67.9)	8.7(8.6)	2.5(2.5)	2.9(2.8)

Selected Spectroscopic Data

$[Ag(8\text{-}OPhVPy)_2][DOS]$-$^1H$ NMR: 250 MHz, $CDCl_3$:



$^{-}O_3SO—CH^K_2—CH^L_2—(CH^M_2)_9—CH^N_3$

8.65 (AA′XX′, 4H, H^A, $J = 6.7$, 0.1 Hz),
7.30 (AA′XX′, 4H, H^E, $J = 8.9$, 0.2 Hz),
7.24 (AA′XX′, 4H, H^B, $J = 6.8$, 0.1 Hz),
7.16 (AB, 2H, $H^{C/D}$, $|J| = 16.1$ Hz),
6.78 (AA′XX′, 4H, H^F, $J = 9.0$, 0.2 Hz),
6.67 (AB, 2H, $H^{C/D}$, $|J| = 16.1$ Hz),
4.18 (*t*, 2H, H^K, $J = 6.6$ Hz), 3.95 (*t*, 4H, H^G, $J = 6.6$ Hz),
1.77 (*m*, 6H, $H^{H/L}$), 1.22 (*m*, 28 H, $H^{I/M}$),
0.90 (*t*, 6H, H^J, $J = 6.6$ Hz), 0.86 (*t*, 3H, H^N, $J = 7.0$ Hz).

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