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Liquid Crystals

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Liquid crystalline complexes of 4-alkoxystilbazoles with silver 1,12-dodecylene disulphate

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A new series of metal complexes of silver(I) 1,12-dodecylene disulphate with 4-alkoxystilbazole ligands has been synthesized. These difunctional silver stilbazole complexes are mesomorphic, showing a nematic phase at short chain lengths and SmA and SmC phases at longer chain lengths. The single crystal X-ray structure of the hexyloxy homologue shows a polymerized arrangement of sulphate-bridged dimers.

1. Introduction

Stilbazole derivatives which bind well to a variety of metal centres [1] have been studied continuously in the field of metallomesogens since the mid-1980s. Of the range of materials studied, complexes of monoalkoxy derivatives with different silver salts, AgX, yielding two-coordination, linear complexes $[AgL_2][X]$ (figure 1) have been investigated extensively as part of this work [2]. These complexes have been shown to exhibit a remarkably rich and diverse mesomorphism, nematic, SmA, SmC, G and cubic phases have all been observed, while in polycatenar derivatives, a range of columnar phases as well as cubic phases, have all been identified. Examples showing lyotropic properties are also known [3]. The liquid crystalline behaviour [2] of these systems depends strongly on the anion [4], the number [5], and length of the stilbazole alkoxy chains [6] and other substituents which may be present on the stilbazole [7]. More recently, isomeric stilbazoles and their complexes with silver(I) have also been investigated [8], as have polycatenar, bent-core systems [9].

Of all the systems studied, those formed from complexation of a stilbazole to a silver alkylsulphate have provided the richest mesomorphism, and some of the more interesting observations are now given. For example, it was shown that for the dodecylsulphate (DOS) salts (figure 1, $X=C_{12}H_{25}OSO_3$), for $n<6$, N and SmA phases were formed, while for $n\geq6$, SmA, SmC and cubic phases were observed [10]. The pattern of observing N phases at short ligand chain lengths and SmA and SmC phases at longer ligand chain lengths was common to all the systems with alkylsulphate anions, but the cubic phase was observed only when the alkylsulphate chain was dodecylsulphate or longer [2]. The length of the alkylsulphate chain was also shown to be important in polycatenar derivatives, where the interplay between ligand and anion chain lengths determined whether cubic or columnar phases were observed [4 *c*]. Detailed studies by X-ray diffraction (XRD) and dilatometry allowed a mechanism to be proposed for the columnar-to-cubic transition in these polycatenar systems [5 *a*].

One very curious observation made in the mesomorphism of the alkylsulphates of 4-alkoxystilbazoles related to the point in the phase diagram at which a SmA phase was seen for the first time. This is illustrated by reproducing the phase diagram for the octylsulphate complexes (figure 2) Thus, at short chain lengths, only a nematic phase is seen but at the first chain length where a SmA phase was observed, the following phase sequence was found: I • N • SmA • N_{re} • SmC. In this sequence, N_{re} represents a *re-entrant* nematic phase which appears 'out-of-sequence' below the SmA phase;

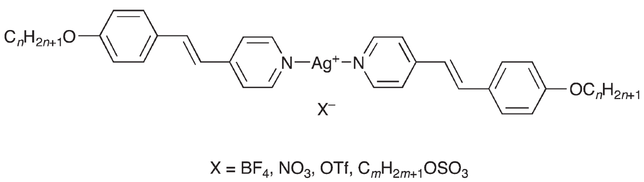

Figure 1. Structure of silver(I) complexes of 4-alkoxystilbazoles.

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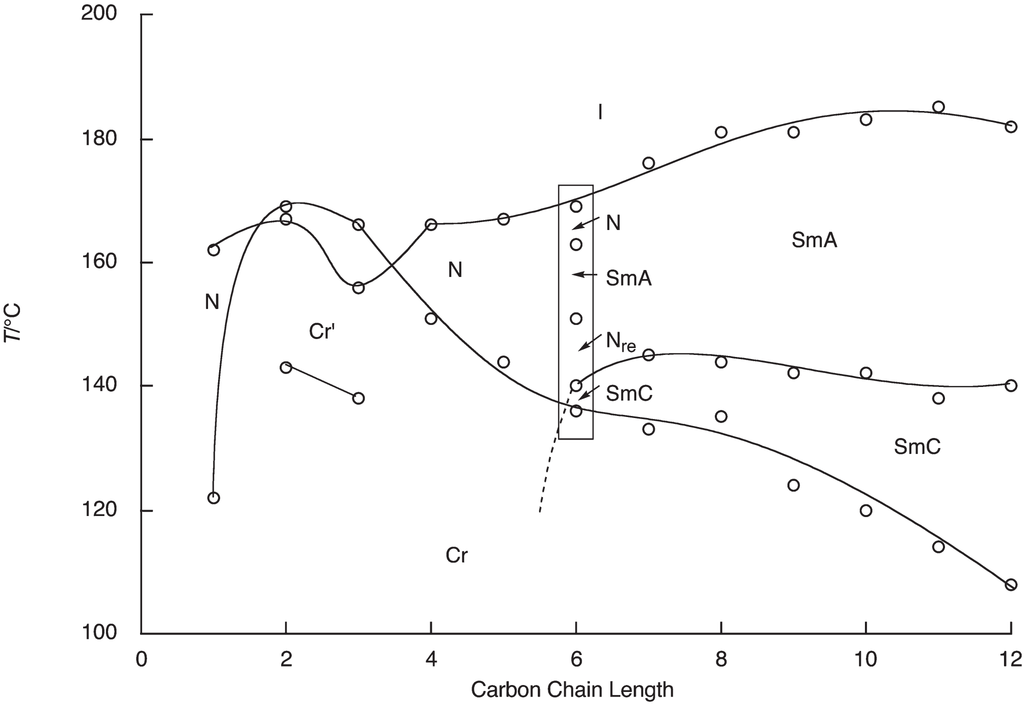

Figure 2. Phase diagram for the complexes [Ag(4-alkyloxystilbazole)$_2$][$C_8H_{17}OSO_3$].

in other cases, the SmC phase was found monotropically. Re-entrant phases are well-known [11] and are normally associated with a change in intermolecular arrangement. Thus, for example, in strongly polar systems such as cyanobiphenyl mixtures, molecules are arranged in an antiparallel fashion giving rise to a nematic phase, below which is a SmA phase. However, the nature of the antiparallel arrangement can change on cooling through the SmA phase and in this new arrangement, a nematic phase is possible, giving rise to the cooling phase sequence: I • N • SmA • N_{re}. XRD studies of one silver octylsulphate complex with its N_{re} phase, showed that it possessed strong, cybotactic SmC fluctuations; which is to say that prior to transition from N_{re} to SmC, there were SmC-like domains present within the N_{re} phase [12].

The origin of the N_{re} phase in these silver complexes is unclear, but in a single crystal structure determination of an octylsulphate salt, it was found that the complex existed as a dimer with two sulphate groups acting to bridge the Ag_2 unit (figure 3) [13]. Clearly then, one possibility would be that this dimer could rearrange into a monomeric motif and that this new species would also be mesomorphic giving rise to re-entrant behaviour. Attempts to observe this behaviour experimentally using EXAFS and ^{109}Ag MAS NMR spectroscopy have been unsuccessful, the former due to the X-ray absorptivity of silver.

To date, studies of stilbazoles and their metal complexes have been confined to simple, monomeric materials precursors with two exceptions (figure 4). In one, Kato [14] reported polymeric materials based on dimeric stilbazoles complexed to silver(I), while in the other, we reported dimeric complexes of Ir^{I} based on similar dimers [15]. Thus, given the significance of the alkylsulphate chain in the mesomorphism of silver complexes of this general type, we undertook to investigate a series of materials in which alkoxystilbazoles are bound to disilver alkylenedisulphates. The results of these studies are now reported.

2. Synthesis

The ligands were prepared by literature methods [16], while disilver(I) 1,12-dodecylene disulphate was obtained as illustrated in figure 5. A C_{12} chain was used in the spacer to give some analogy to the work we have carried out previously with dodecylsulphate [2]. Thus, disodium-1,12-dodecylene disulphate was prepared by the reaction of chlorosulphonic acid with 1,12-dodecanediol in ether, followed by treatment with sodium hydroxide to give the sodium salt in effectively quantitative yield. The disilver dodecylene disulphate was then obtained in 57% yield by precipitation, after mixing an aqueous solution of silver nitrate and the sodium salt. The final complex was prepared by reaction of four equivalents of the ligand with the disilver dodecylene disulphate in dichloromethane at room temperature, and was obtained as an off-white solid in yields of around 50%.

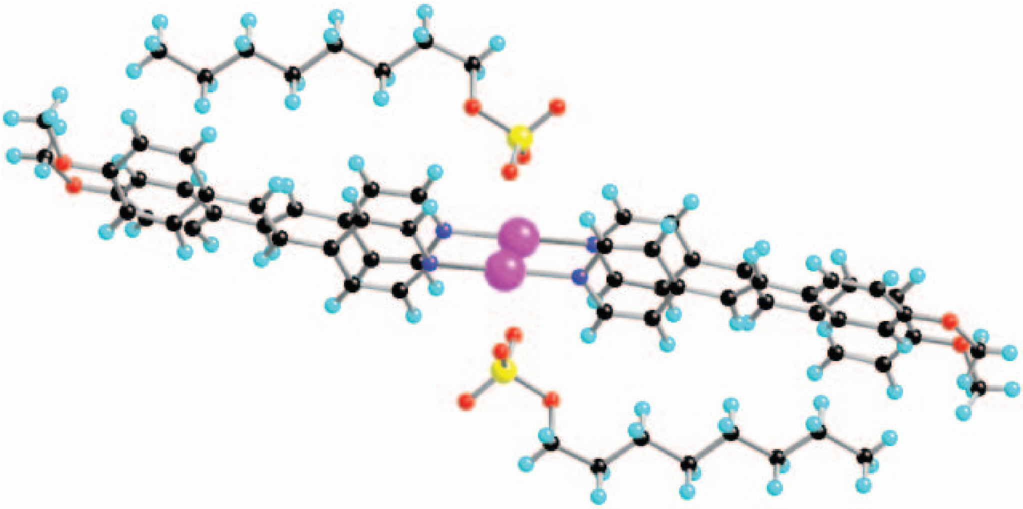

Figure 3. X-ray structure of bis(4-methoxy-4′stilbazole)silver octylsulphate.

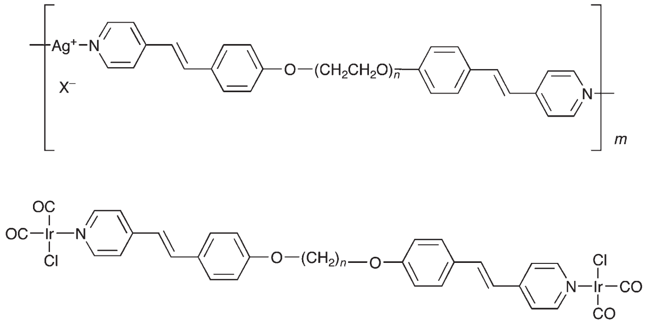

Figure 4. Structure of polymeric and dimeric stilbazole complexes.

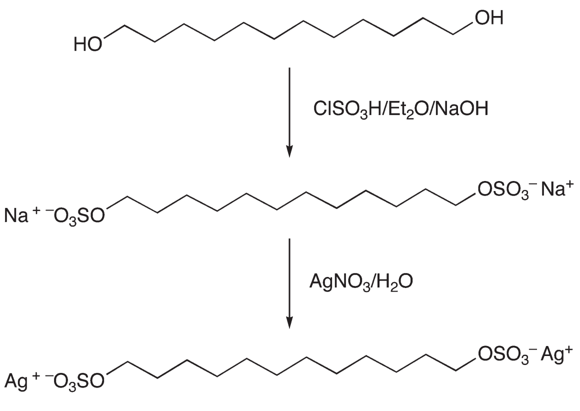

Figure 5. Preparation of silver(I) 1,12-dodecylene disulphate.

The ^1H NMR spectra of the complexes showed the expected aromatic pattern for the ligands, namely the two $AA'XX'$ spin systems of the phenyl and pyridyl rings, plus the AB system for the vinyl link which indicated a *trans*-geometry by virtue of the observed coupling constant ($J_{AB} = 16.1$ Hz). The integrity of the complex was indicated by the integration of the signals at δ 4.24 (4H–CH_2 next to the sulphate oxygen) and δ 4.06 (8H–CH_2 next to the phenate oxygens), showing a ratio of two bis(stilbazole)silver cations to each dodecylene disulphate dianion.

3. Crystal and molecular structure of the hexyloxystilbazole derivative

In order to gain more information on the arrangement of these materials in the solid state, single crystals were obtained for one homologue and the structure solved. Thus, colourless blocks of $[Ag(butyloxystilbazole)_2]_2[O_3SO(CH_2)_{12}OSO_3]$ were crystallized from THF/hexane and found to exist in the triclinic space group P–1. Crystal data are collected in table 1. There is a little disorder present in the structure including the water molecule whose hydrogen atoms were restrained.

The structure (figure 6) showed the same Ag_2 motif found in the octylsulphate complex described above (figure 3) in which the two silver atoms are ‘supported’ by two κ^2-sulphate groups. However, unlike the octylsulphate that has two independent ‘dimer’ units, the structure contains only a single repeating unit. Further, while the octylsulphate complex is a hemihydrate, in this complex there is one water to each silver atom and the water is hydrogen-bonded to a sulphate oxygen (in either disordered state). However, there is no neighbouring sulphate oxygen in the present structure and so the water does not form part of the polymeric arrangement. The Ag–Ag separation (3.2818(15) Å) is slightly longer than the two distances for the octylsulphate complex (3.193(2) and 3.210(2) Å), but still well within the limits of known Ag–Ag close contacts [17]. The Ag–$O_{sulphate}$ distances are slightly shorter (2.710(3) and 2.754(3) Å) compared with

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{80}H_{104}Ag_2N_4O_{14}S_2$	
Formula weight	1625.53	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P-1$	
Unit cell dimensions	$a = 7.82870(10)$ Å	$\alpha = 89.6820(10)^\circ$
	$b = 15.8281(3)$ Å	$\beta = 83.9250(10)^\circ$
	$c = 16.2118(3)$ Å	$\gamma = 78.8630(10)^\circ$
Volume	1959.73(6) Å^3	
Z	1	
Density (calculated)	1.377 Mg/m^3	
Absorption coefficient	0.618 mm^{-1}	
$F(000)$	850	
Crystal	Block; Colourless	
Crystal size	$0.30 \times 0.20 \times 0.15$ mm^3	
θ range for data collection	2.93−25.03°	
Index ranges	$-9 \le h \le 9$, $-18 \le k \le 18$, $-19 \le l \le 19$	
Reflections collected	17258	
Independent reflections	6475 [$R_{\text{int}} = 0.0395$]	
Completeness to $\theta = 25.03^\circ$	93.4%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9131 and 0.8364	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	6475/0/480	
Goodness-of-fit on F^2	1.046	
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1 = 0.0505$, $wR2 = 0.1344$	
R indices (all data)	$R1 = 0.0601$, $wR2 = 0.1422$	
Largest diff. Peak and hole	1.110 and −0.917 e Å^{-3}	

(2.745(5), 2.772(5), 2.891(5) Å and 2.926(5) Å) in the octylsulphate system, suggesting a better packing; while the Ag–N_{py} distances are comparable (2.155(3) and 2.158(3) against 2.138(6), 2.151(6), 2.152(6) and 2.157(6) Å). Note that the sulphate group is disordered over two sites and that, in common with the silver octylsulphate structure, there is a disordered water molecule in the structure associated with the sulphate oxygens; these oxygens, along with one part of the disordered sulphate, are omitted from the figures. In fact, there appear to be two (low energy) positions for which the sulphate can coordinate to the silver atoms and the water. Doubling axes to try to see if the disorder is in some way 'ordered', e.g. alternating between the two positions, does not help, and the sulphate disorder is always observed. The same is true of for the small amount of disorder found in the terminal alkyl chain.

However, perhaps the most striking feature of the structure is the fact that, arranged as a local Ag_2 dimer, the complexes necessarily form a polymeric arrangement with the Ag_2 unit being bridged by sulphate groups from two different alkylene disulphates, as shown in figure 7 and schematically in figure 8 (*a*). Thus, in stark contrast to the situation in the octylsulphate material, the anion chain is constrained in its movement as it is, in effect, the backbone to a main chain polymer comprising laterally attached mesogenic groups, figure 8 (*b*). Nevertheless, a structural feature common to this complex and to the

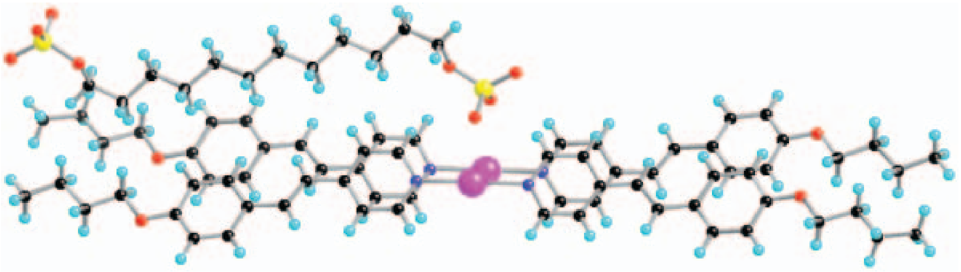

Figure 6. Structure of the unsymmetric unit of the silver complex with $n = 4$.

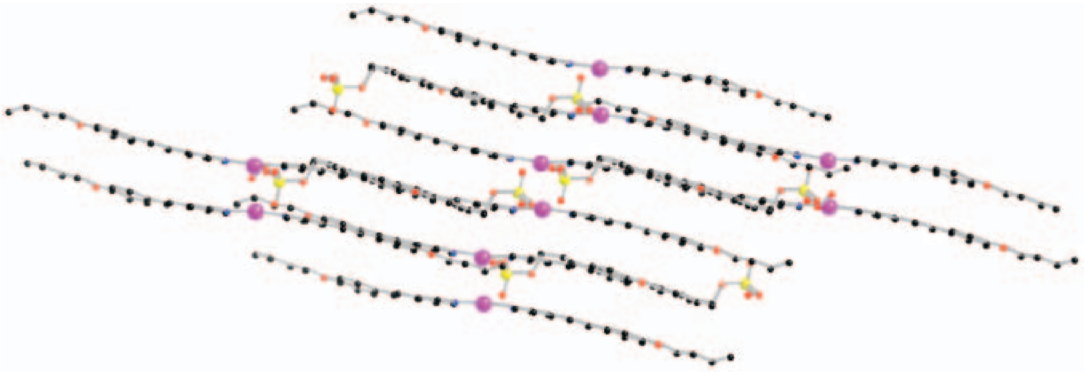

Figure 7. Packing diagram to illustrate the polymeric nature of the complexes in the solid state.

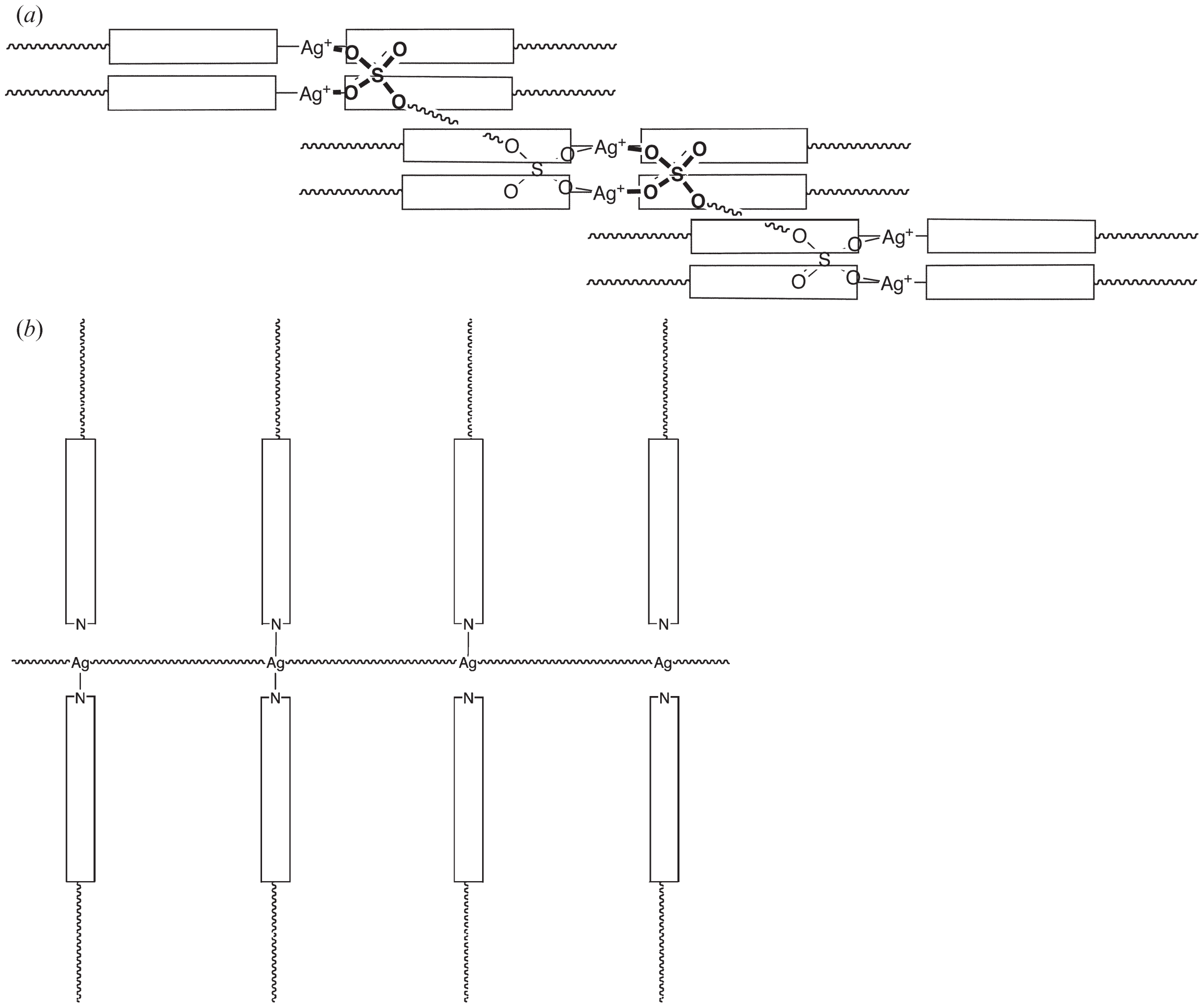

Figure 8. (*a*) Schematic diagram to illustrate the polymeric arrangement referred to in figure 7; (*b*) schematic to show disfavoured arrangement of the silver polymers.

octylsulphate salt which had previously been characterized crystallographically, is that the anion chain extends along the side of the molecule.

4. Mesomorphism

The mesomorphism was studied by polarizing optical microscopy (POM) and differential scanning calorimetry

(DSC), and the mesophases were assigned on the basis of optical textures; the transition temperatures and thermal data for these complexes are collected in table 2, while the phase diagram is shown in figure 9. A general observation made here and discussed later is the fact that although formally polymeric, at least in the crystalline state, the viscosity of the mesophases and the ease with which textures are formed is not really reminiscent of a polymer, but of a conventional, low-molar-mass compound.

Of the complexes studied, only the methoxy homologue was non-mesomorphic and it melted directly to the isotropic phase at 233°C with no sign of a monotropic phase on melting. However, for $n=2$, 4 and 5, the complexes showed monotropic nematic phases at 196, 184 and 180.5°C, respectively, identified (figure 10) by the presence of two- and four-brush isogyres and by the characteristic flashing seen on mechanical disturbance of the sample. The ethyloxy homologue, however, showed extensive decomposition on clearing. For the hexyloxy homologue, melting of the solid gave way to a nematic phase at 175°C, the transition being marked by the appearance of the characteristic fingerprint texture. The nematic phase cleared at 180°C.

Table 2. Thermal data for the tetra(4-alkoxy-4′-stilbazoles)-dissilver(I) 1,12-dodecylene disulphate complexes. The absence of thermal data indicates a second-order transition in all cases except in the case of the monotropic N–M transition ($n=7$) where the event was seen by microscopy and not by DSC.

n	Transition	T/°C	ΔH/kJ mol^{-1}
1	Cr–I	233	103.4
2	Cr–I	199	81.4
	(I–N)	(196)	—
4	Cr_1–Cr_2	169	42.4
	Cr_2–I	184	42.7
	(I–N)	(180)	(−2.5)
5	Cr_1–Cr_2	126	35.6
	Cr_2–I	185	71.8
	(I–N)	(180.5)	(−0.7)
6	Cr_1–Cr_2	122	48.3
	Cr_2–Cr_3	162	39.2
	Cr_3–N	175	18.4
	N–I	180	1.7
7	Cr_1–Cr_2	127	67.9
	Cr_2–SmA	160	26.5
	SmA–I	197	6.8
	(SmA–N)	(143)	—
	(N–M)	(139)	—
8	Cr–SmA	163	93.9
	SmA–I	193	10.1
	(SmA–SmC)	(126)	—
10	Cr–SmA	166	108.2
	SmA–I	211	10.4
	(SmA–SmC)	(110)	—
11	Cr–SmA	164	101.0
	SmA–I	213	14.9
	(SmA–SmC)	(108)	—
12	Cr–SmA	149	103.4
	SmA–I	221	16.7
	(SmA–SmC)	(110)	—
14	Cr–SmA	98	52.1
	SmA–SmC	119	2.8
	SmA–I	207	10.5

The behaviour of the heptyloxy derivative is noteworthy as this is the first complex in which a lamellar phase appears (SmA, figure 11). Thus, on melting at 160°C, a SmA formed which persisted until 197°C where it cleared. Cooling reformed the SmA phase, but at 143°C the texture of a nematic phase appeared monotropically (figure 12). The range of this nematic phase was quite short and at 139°C, a mosaic texture formed (figure 13), characteristic of a crystal smectic phase. Unequivocal identification of this phase was not possible in this study, but its texture suggests that it is probably either the crystal smectic G or J phase. The monotropic nematic phase will be discussed below.

At all longer chain lengths, the behaviour followed the same pattern, as the compound melted to give rise to a SmA phase which then cleared to the isotropic phase. On cooling, the SmA phase re-formed, but the crystal phase did not readily reappear and so a monotropic SmC phase was seen between 45 and 50°C below the melting point. The only exception to this behaviour was for $n=14$, where the crystal phase stability dropped markedly, allowing the SmC phase to be seen enantiotropically. With the exception of the SmC–SmA transition in the tetradecyloxy homologue, all other SmA–SmC transitions were found to be second order.

Consideration of the phase diagram as a whole (figure 9) shows that the crystal phase decreased in stability from $n=1$ to $n=7$, after which it remained approximately constant until it started to decrease steeply around $n=12$, falling from its plateau of about 160°C to about 100°C at $n=14$. In contrast, there was little variation in the stability of the SmA phase increased with ligand chain length, increasing from 197°C at $n=8$ to 221°C at $n=12$, before falling slightly to 207°C at $n=14$. In the case of the SmC phase, these was little variation in the phase stability, which ranged from 108 to 126°C. A nematic phase (excluding the monotropic N phase) was seen in four of the materials studied and dropped in stability from the ethyloxy to the butyloxy homologue after which it remained approximately constant.

5. Discussion

It is of interest then to compare the mesomorphism of these new complexes containing a dodecylene

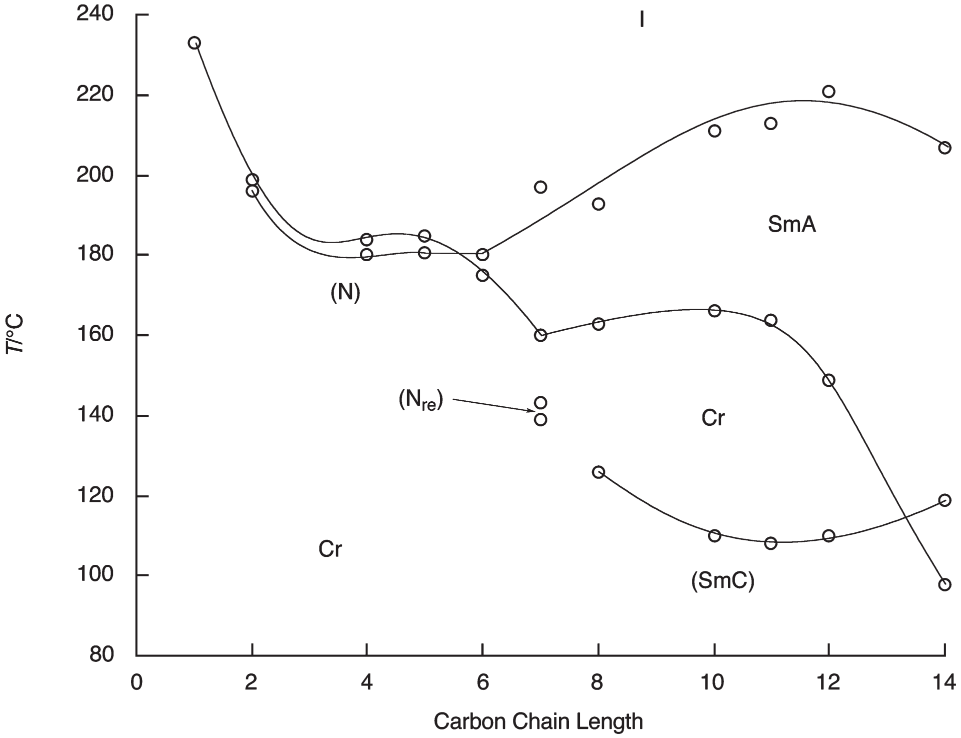

Figure 9. Phase diagram of the silver dodecylenedisulphate complexes.

disulphate anion, with the behaviour of complexes of a simple dodecylsulphate, and to speculate on the nature of the species giving rise to the mesophase. In general terms, the transition temperatures of the new complexes are appreciably higher than those of the related (mono)alkyl sulphates, although many general features of the mesomorphism are the same. Thus, there is a nematic phase at shorter terminal chain lengths which gives way to SmA and SmC phases as the chain length increases. The cubic phase is, however, absent and this point will be revisited.

One of the interesting features of these materials is that the trends in phase behaviour with ligand chain length mirror those of simple, low-molar-mass materials with a nematic phase at short chain lengths, giving way to smectic phases as the chain length increases. Thus, despite the presence of the flexible dianion, the mesomorphism is still driven by the *stilbazole* chain length. This suggests something about the behaviour of the anion dodecylene chain, for it supports the idea that in the mesophase, the chain remains more or less parallel to the bis(stilbazole)silver(I) cation as found in the crystal structure (figures 6 and 7). In this structural sense, it mimics the behaviour of the anion chain in the simple alkyl (mono)sulphate salts and, therefore, precludes an open 'H'-type arrangement, figure 8 (*b*), that would contain too much free volume which would be difficult to fill. An H-shaped arrangement would also present a problem in understanding how the *ligand* chain length determines the mesomorphism, given the separation of the rigid cores. However, the fact that each end of the anion chain is effectively tethered to a cationic unit constrains its motion, and so the counter-play of stilbazole and anion chains must be considered carefully in explaining the mesomorphism.

It is then a relatively straightforward matter to explain the appearance of smectic phases in these materials, for a layered arrangement appears almost to be required by the presence of the bridging dianion. Further, while it is often misleading to draw direct analogies between solid state packing and mesomorphism, it is noticeable from the cartoon in figure 8 (*a*) and from the packing diagram in figure 7 that a layered structure exists, and the flexibility of the dianion chain clearly permits both orthogonal and tilted phases to be observed. The positioning of the alkylene chain is important in other respects, too, for clearly it allows neighbouring cations to 'know' about one another, by virtue of the fact that an increase in the stilbazole chain length does indeed lead to the formation of lamellar phases by what must be microsegregation. Thus, in the absence of longer ligand chains, nematic phases are formed as the effect of the lateral chain dominates and so we would suggest that the alkylene chain has more motional freedom in the nematic phase.

Previously, in discussing the mesomorphism of the

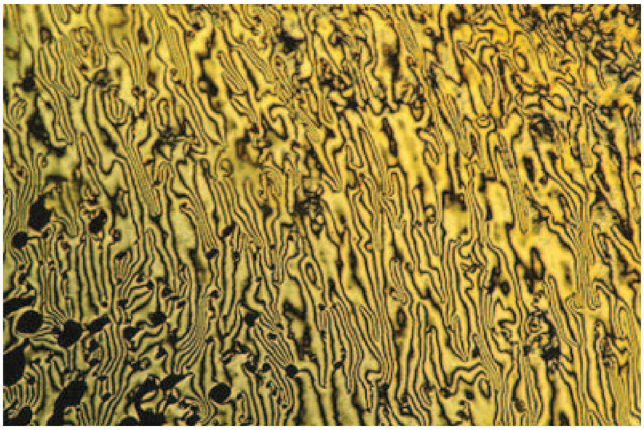

Figure 10. Texture of the nematic phase of the pentyloxy homologue at 145°C.

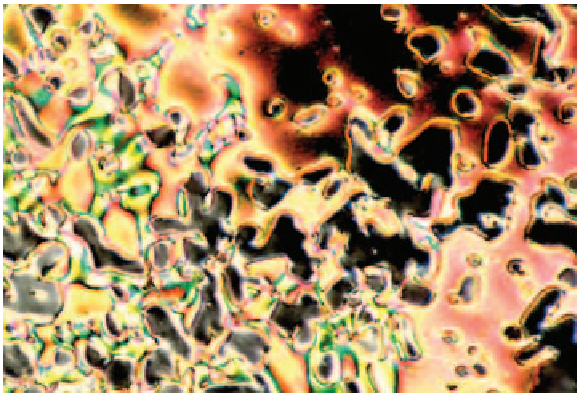

Figure 11. Texture of the SmA phase of the heptyloxy homologue at 164°C on nylon-coated slides.

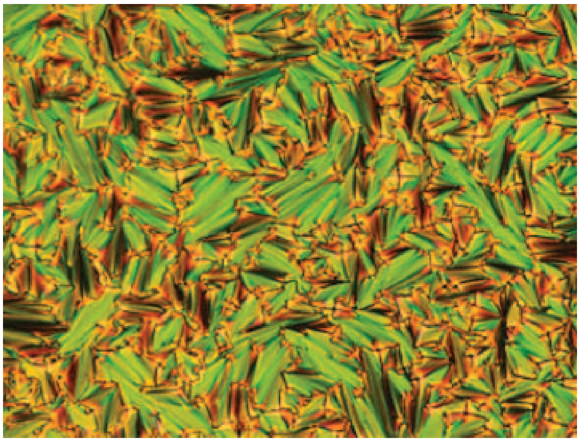

Figure 12. Texture of the N_{re} phase of the heptyloxy homologue at 140°C.

silver salts of alkyl (mono)sulphates, Levelut [12] had argued that the nematic phase in these formally ionic materials was explained by the presence of the flexible, lateral chain, behaviour seen commonly in mesogens of this general type [18]. Smectic phase formation at longer chain lengths then required the presence of intermolecular, electrostatic interactions ($Ag^{+}\cdots{}^{\delta-}[O–S–O]^{\delta-}\cdots Ag^{+}$) in conjunction with microphase separation to overcome the layer-destabilizing effect of this lateral chain. This explanation of lamellar phase

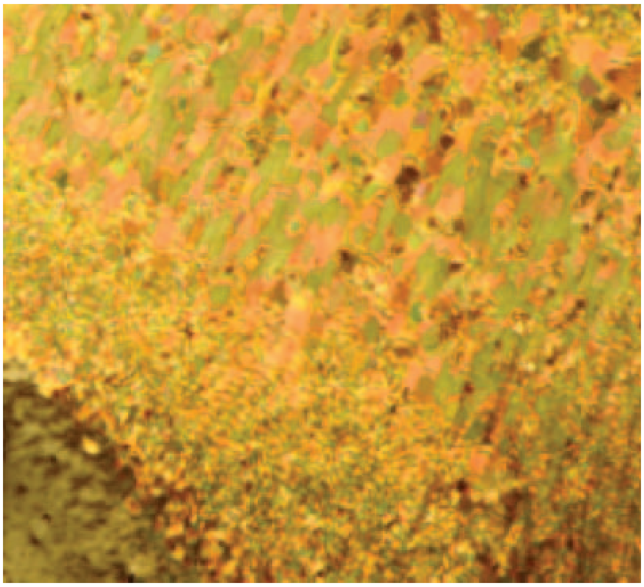

Figure 13. Texture of the mosaic phase forming from the N_{re} phase.

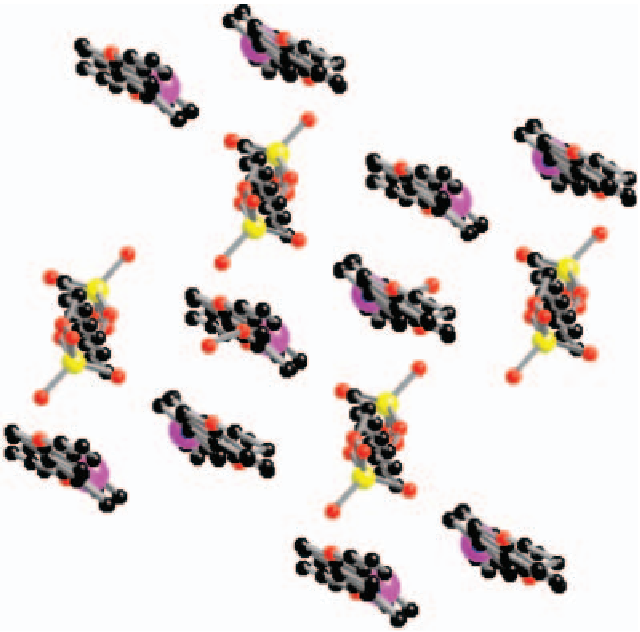

Figure 14. End-on view of the silver complexes to show the separation of the dimeric cation units.

formation clearly cannot apply in the present situation where such intermolecular interactions are precluded on steric grounds (figure 14).† However, the efficient packing of the lateral chain 'bound' to two silver cations and driven by the increase in the stilbazole chain length which promotes microsegregation, leads naturally to a smectic phase. Further, the fact that the dianion chains essentially lubricate the area between the cations may well explain the rather low apparent viscosity of these complexes.

We next consider the cubic phase. In monomeric complexes with alkyl (mono)sulphate chains containing twelve atoms or more, cubic phases are seen when the ligand chain length has a minimum of six carbon atoms. There is good evidence from this work and from related studies of polycatenar silver complexes [2] that an important feature in the appearance of the cubic phase is the balance between the volume of the core and the volume occupied by the terminal chains [19]. Further, when the anion chain is long enough, it can extend beyond the core of the cation and effectively become part of the terminal chain volume, so affecting advantageously these packing parameters which favour cubic phase formation [20]. However, in these dimeric materials, the 'end' of the anion chain is motionally constrained as it is bound to another silver dimer and so is not free to become part of the terminal chain volume. In addition, it can be considered that each alkylene chain has only six of its carbon atoms associated with each bis(stilbazole)silver(I) cation, so reducing greatly its contribution to the volume of the core. Further, we have proposed that the existence of specific intermolecular associations are also necessary for cubic phase formation [20, 21], but as we have argued already, these are precluded in these new complexes and a much more flexible situation pertains. The combination of the above arguments is then consistent with the absence of the cubic phase in these materials.

Finally, we consider the heptyloxy homologue which is the first homologue for which a smectic phase is seen. Heating the crystalline material shows only a SmA phase on heating, which simply clears with no evidence for a nematic phase above it. On cooling, the SmA phase supercools below the melting point and at 143°C, a nematic phase appears which gives way to a crystalline smectic phase at 139°C. While shorter chain length homologues showed a nematic phase which was in many cases monotropic, *this* monotropic phase is clearly different inasmuch as it appears *below* a SmA phase. As such, the behaviour of this homologue is analogous to other mesomorphic silver alkylsulphates which we have studied, in that the first homologue to show a smectic phase shows a nematic phase below that smectic phase. However, in all the other systems we have studied, this nematic phase has been properly re-entrant as it has appeared twice—once above the SmA and once below it. But, in this case there is no nematic phase above the SmA and so it cannot be argued that the phase we observe is re-entrant. So how might its formation be understood?

In the case of the silver complexes of (mono)alkylsulphates, and in the present case with dodecylenedisulphate anions, we have suggested that it is the stilbazole chain length which drives the introduction of lamellar phases. Where simple alkylsulphates are concerned, the microphase separation induced by the increasing length of the stilbazole chain has to overcome the structurally disruptive influence of the lateral chain, a process aided by electrostatic cation–anion–cation interactions that result from this more ordered arrangement. In the case of the dodecylenedisulphates, the lateral chain also represents a structurally disruptive influence, and in overcoming this and arriving at microphase separation, the system requires a more efficient arrangement of the anion chain and so space is filled more effectively. In each case, therefore, microphase separation results when opposing, structurally disruptive influences are resolved, and so lamellar phase formation can be considered as the prevalence of microphase separation. It is not unreasonable, therefore, to recognize that in the particular homologue where these opposing influences are most in 'conflict', the situation is finely balanced and so a nematic phase can be seen out of sequence. Whether this behaviour results from a change from a dimeric to a monomeric arrangement is, at present, unclear, and given the resistance of these silver complexes to study by X-ray and NMR methods, it is not clear how this behaviour may be elucidated precisely, and the presence (or otherwise) of monomers and dimers confirmed.

One last aspect of this work deserves a few words of comment. In the search for materials with the elusive biaxial nematic phase [22], there is good experimental evidence for its existence in a series of polymers in which a rod-like, mesogenic moiety is attached to the polymer chain laterally via a flexible spacer [23]. In these materials, it has been argued that the biaxiality arises from a restricted rotation of the rod-like mesogenic part about its long axis, due to the constraining influence of the lateral chain by which it is attached to the polymer. This then leads us to

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† That intermolecular, electrostatic interactions are not required to explain the behaviour of the dodecylene disulphate salts does not contradict their existence in the case of monoalkylsulphate salts, for in this latter case, they are an integral part of a consistent argument applied to understand the existsnce of the cubic phase. This is discussed fully in references [2, 12, 20, 21].

examine these new silver complexes where it has been suggested that the arrangement of the rod-like cations constrained by the alkylene disulphate dianions presents a similar situation [24]. In fact, the nematic phases of these new silver complexes are not easily studied due to their monotropic nature, but in all cases, we observe schlieren textures with four-brush isogyres. Thus, while the presence of only two-brush isogyres does not prove the existence of a biaxial nematic phase [25], the observation of four-brush isogyres [26] does, however, appear to preclude it!

6. Experimental

All solvents and 4-methylpyridine were distilled prior to use according to standard procedures [27]. Thus, dichloromethane was distilled from calcium hydride, tetrahydrofuran from sodium and benzophenone, and toluene from sodium. 4-Methylpyridine was distilled over sodium hydroxide and stored over sodium hydroxide pellets. All other chemicals were used as supplied.

Proton and carbon NMR spectra were recorded on a Bruker DFX 400 MHz spectrometer. Elemental analyses were performed at the School of Chemistry University of Exeter (microanalytical data for the complexes are given in table 2). Analysis by DSC was carried out using a Perkin-Elmer DSC7 instrument using various heating rates. Mesomorphism was studied by hot stage polarizing microscopy using a Zeiss Labpol microscope equipped with a Linkam TH600 hot stage and PR600 temperature controller. All of the mesophases were assigned by their optical textures.

Single crystals of the silver complex was obtained from solution in THF by slow addition of hexane. Suitable crystals were selected and data collected on a Bruker Nonius KappaCCD Area Detector at the window of a Bruker Nonius FR591 rotating anode ($\lambda_{\text{Mo-K}\alpha}$ = 0.71073 Å) driven by COLLECT [28] and DENZO [29] software at 120 K. Structures were determined in SHELXS-97 [30] and refined using SHELXL-97 [31].

6.1. *Synthesis of sodium-1,12-dodecylene disulphate*

Chlorosulphonic acid (3 g, 25.2 mmol) was added dropwise to a flask containing diethyl ether (50 cm^3), and the mixture was left to stir for a few mins. Dodecan-1,12-diol (2.55 g, 12.6 mmol) in diethyl ether (20 cm^3) was then added to the solution and the stirring was maintained for 30 mins. The solvent was evaporated *in vacuo* and the residue dissolved in ethanol (100 cm^3, 95%v/v). Sodium hydroxide (1 g, 25.2 mmol) was added, and the mixture stirred for 5 h. The white precipitate was filtered, washed thoroughly with absolute ethanol, and then with diethyl ether. After being air-dried, the sodium salt, obtained in good yield (5.1 g, 99%), was suitable to use for the next step.

6.2. *Synthesis of silver 1,12-dodecylene disulphate*

Sodium-1,12-dodecylene disulphate (5.1 g, 12.5 mmol) dissolved in warm water (50 cm^3) was added to an aqueous solution of silver nitrate (4.25 g, 25 mmol) and the resulting mixture stirred in a vessel protected from light for 2 h. The precipitate was filtered, washed with cold water and dried under high vacuum. The yield was 57% (4.1 g, 7.1 mmol).

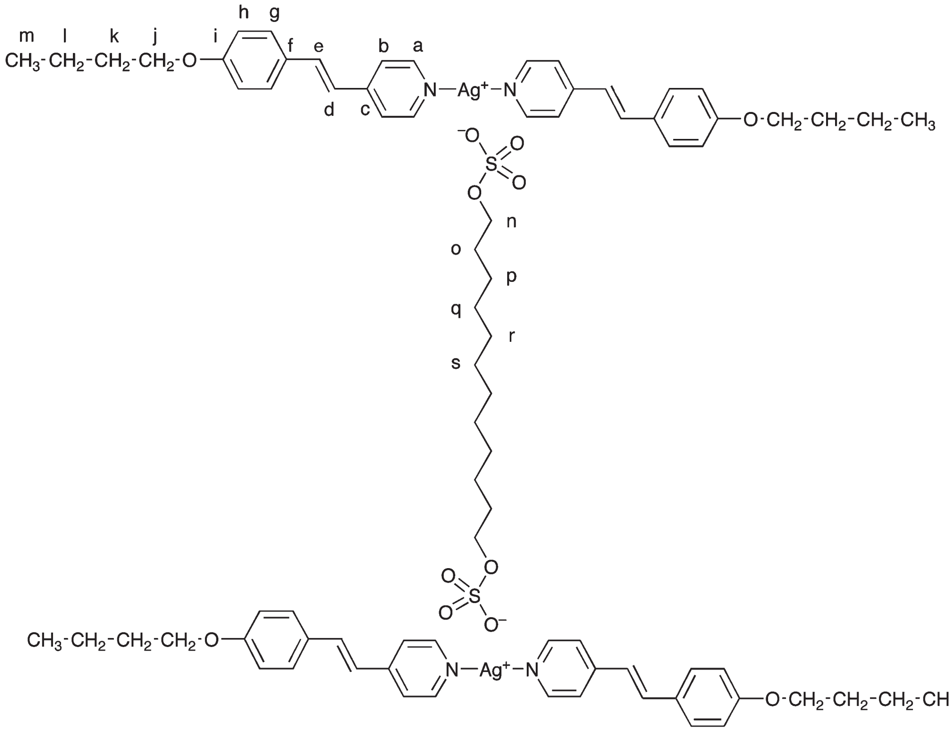
6.3. *Synthesis of tetra(4-alkoxy-4′-stilbazole)silver(I)-1,12-dodecylene disulphate*

All homologues were prepared by the same method as described below for the butyloxy complex and complete analytical data are given in table 3. A suspension of silver 1,12-dodecylene disulphate (0.116 g, 0.2 mmol) in dichloromethane (20 cm^3) was placed in a flask protected from light. 4-Butyloxy-4-stilbazole (0.202 g, 0.8 mmol) dissolved in dichloromethane (20 cm^3) was added dropwise and the mixture was stirred at room temperature overnight. The resulting transparent solution was filtered through Celite to remove any unreacted silver salt. The solvent was evaporated at 40°C and the solid crystallized from hot methanol yielding a slightly yellow solid (0.152 g, 0.096 mmol, 48%). Some homologues were crystallized from a mixture of methanol and dichloromethane.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.71 (8H, *AA′XX′*, Ha, J = 6.09 Hz), 7.40 (8H, *AA′XX′*, Hg, J = 8.68 Hz), 7.31 (8H, *AA′XX′*, Hb, J = 6.09 Hz), 7.22 (4H, *AB*, He, $^3J_{\text{HH}}$ = 16.12 Hz), 6.86 (8H, *AA′XX′*, Hh, J = 8.68 Hz), 6.75 (4H, *AB*, Hd, $^3J_{\text{HH}}$ = 16.12 Hz), 4.24 (4H, *t*, Hn, $^3J_{\text{HH}}$ = 6.07 Hz), 4.06 (8H, *t*, Hj, $^3J_{\text{HH}}$ = 6.54 Hz), 1.77 (8H, *m*, Hk), 1.68 (4H, *m*, Ho), 1.50 (8H, *m*, Hl), 1.37 (4H, *m*, Hp), 1.23 (4H, *m*, Hq), 1.14 (8H, *m*, Hr, Hs), 0.98 (12H, *t*,

Table 3. Analytical data for the tetra(4-alkoxy-4′-stilbazoles)dissilver(I) 1,12-dodecylene disulphate complexes.

		Calculated (found)/%		
n	Yield/%	C	H	N
1	70	57.4 (56.8)	5.4 (5.1)	3.9 (3.5)
2	61	58.5 (57.8)	5.7 (5.5)	3.8 (3.6)
4	48	60.5 (60.1)	6.3 (6.3)	3.5 (3.4)
5	65	61.3 (61.3)	6.6 (6.6)	3.4 (3.1)
6	59	62.1 (62.0)	6.9 (6.9)	3.3 (3.1)
8	75	63.5 (63.1)	7.3 (7.5)	3.1 (2.9)
10	56	64.8 (64.3)	7.7 (7.8)	2.9 (2.7)
11	50	65.4 (64.7)	7.9 (8.0)	2.8 (2.6)
12	90	66.0 (65.9)	8.1 (8.3)	2.8 (2.6)
14	73	67.0 (67.3)	8.4 (8.6)	2.6 (2.4)



Hm, ${}^{3}J_{\mathrm{HH}}=7.24$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1 (i), 152.2 (a), 147.1 (c), 135.0 (e), 128.8 (g), 127.9 (f), 122.0 (d), 121.3 (b), 114.8 (h), 67.9 (n), 67.8 (j), 31.3 (o), 29.6, 29.5, 29.3, 26.0 (k, p, q, r, s), 19.2 (l), 13.9 (m).

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