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Effect of alkyl sulfate anion on the mesomorphism of 3,4-dialkoxystilbazole complexes of silver(I)

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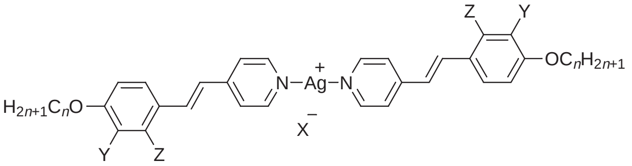
3,4-Dialkoxystilbazoles have been complexed to silver(I) alkyl sulfates in which the alkyl sulfate chain length has been varied. The mesomorphism of the materials is dominated by the formation of cubic and columnar phases, and the alkyl sulfate chain length is shown to affect the mesophase range and type. The mesomorphism of these, and related, stilbazole complexes of silver alkyl sulfates is discussed in terms of the effect of aromatic/paraffinic interfacial curvature and the effects of ionic interactions.

Introduction

In the last 10–15 years, the literature on metallomesogens has increased hugely and has been well reviewed.[1] Since initial studies on largely flat and linear complexes, the range of materials found to be capable of showing liquid crystal properties has grown substantially and numerous different metals have now been incorporated successfully into mesogenic systems. In these studies, it is of interest both to define an increasing number of metal/ligand possibilities for the realisation of metallomesogens, and also to undertake systematic investigations of the structure/property relationships so that understanding, and ultimately prediction, of mesomorphic behaviour will arise.

We have worked extensively with silver(I) complexes of monoalkoxystilbazoles (**1**; Fig. 1[2–7]), and more recently on mesomorphic, tetracatenar complexes based on dialkoxystilbazoles (**2**; Fig. 1).[8] In this work, we have started to accumulate a substantial amount of data relating structure to property, particularly in relation to cubic phases. As an extension of this work, we now report the results of a study of the effect of alkyl sulfate chain length on the mesomorphism of silver(I) complexes of 3,4-dialkoxystilbazoles (Fig. 1; **2**).



1 $X = BF_4, NO_3, CF_3SO_3, C_mH_{2m+1}OSO_3$
$Y, Z = H$ or F

2 $X = C_mH_{2m+1}OSO_3$
$Y = OC_nH_{2n+1}$
$Z = H$

Fig. 1 Structure of stilbazole complexes of silver(I)

Results and Discussion

Synthesis and characterisation of the ligands and their complexes

The ligands were synthesised as described previously,[8] and will be abbreviated St(*n*-3,4), where *n* represents the number of carbon atoms in the alkoxy chains. Sodium alkyl sulfates were obtained by reaction of chlorosulfonic acid with the appropriate terminal alcohol in ether, followed by treatment with sodium hydroxide to give the sodium salt in good yield. Silver alkyl sulfates were then prepared by precipitation after mixing aqueous solutions of silver nitrate and the corresponding sodium alkyl sulfate, although silver octyl sulfate and hexyl sulfate could not be prepared in this way, being water soluble.

The bis(3,4-dialkoxy-4′-stilbazole)silver(I) alkyl sulfate complexes were then prepared by stirring two equivalents of the stilbazole with one equivalent of silver alkyl sulfate in dichloromethane at room temperature in the dark for 4 h (Fig. 2a). The products so obtained remained stable for a prolonged period of time when stored at room temperature in the dark. The complexes of silver hexyl- and octyl-sulfate could not be prepared this way, and so were obtained *via* metathesis of the appropriate bis(3,4-dialkoxy-4-stilbazole)silver triflate using sodium hexyl- or octyl-sulfate. The metathesis reaction was performed at reflux in acetone for 12 h in the dark after which the products precipitated out of solution as pale yellow powders (Fig. 2b).

The ligands and complexes were characterised by ^1H and ^{13}C NMR spectroscopy. All the stilbazoles were *trans* about the ethylenic double bond as evidenced by proton NMR, in which the coupling constant of the AB system was *ca.* 16.0–16.5 Hz. The complexes had a similar spectra to the free ligands, although some differences indicated that the complexation had been achieved. For example, the protons on the carbons *ortho* to the nitrogen of the pyridine ring, and the vinylic protons were shifted downfield by a few tenths of ppm, relative to their positions in the spectra of the free ligands,

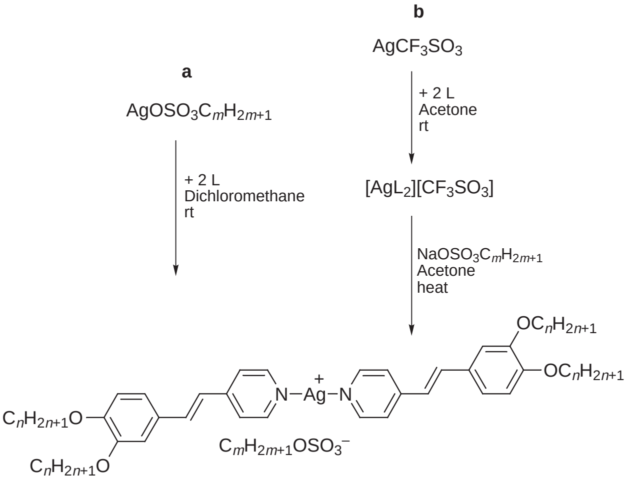


Fig. 2 Synthesis of the complexes under study

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while the carbons *ortho* and *para* to the ring nitrogen were shifted downfield by 2–4 ppm. The complexes were further characterised by the presence of an additional triplet at around 4 ppm due to the OCH_2 protons of the alkyl sulfate anion in addition to the triplets from the alkoxy groups bound to the stilbazole. The purity of the ligands and the complexes was confirmed by elemental analysis.

Effect of alkyl sulfate chain length in complexes of 3,4-dialkoxystilbazoles, $[Ag\{St(n\text{-}3,4)\}_2][C_mH_{2m+1}OSO_3]$

We have already shown that the alkyl sulfate chain length influences dramatically the mesomorphic properties of silver complexes of this general type. For example, silver complexes of 4-alkoxy-4′-stilbazoles with dodecyl- and tetradecyl-sulfate anions showed nematic, S_A, S_C, and cubic phases, while the analogous complexes with decyl-and octyl-sulfate showed only nematic, S_A, S_C phases, with the cubic phase being absent. We rationalised this behaviour in relation to the position of the anion chain relatively to the paraffinic/aromatic interface.[6] Thus, when the anion chain length was short so that it did not extend beyond the aromatic core (octyl- and decyl-sulfate),[3] the cubic phase was absent, but when it extended beyond the interface (dodecyl- and tetra-decylsulfate), the cubic phase was observed. In this present study, therefore, it is of interest to see the effect of the anion chain length on a system where columnar and cubic phases predominate.

It is, therefore, first appropriate to recall the mesomorphism of the complexes $[Ag\{St(n\text{-}3,4)\}_2][C_{12}H_{25}OSO_3]$ which can act as a reference point (Fig. 3). Thus, for $4 \leqslant n \leqslant 10$, a cubic phase was seen while for $6 \leqslant n \leqslant 12$, a columnar hexagonal phase was observed. Melting points were relatively constant at between 55–70 °C, while clearing points varied from 100–170 °C.[8] In these complexes, as in the complexes described below, the mesophases were identified initially by optical microscopy, with both the cubic and columnar mesophases giving characteristic textures. In the latter case, these textures were consistent with the columnar phase having hexagonal symmetry. The mesomorphism in these complexes was finally confirmed using both X-ray diffraction and freeze-fracture electron microscopy.

In order to 'sample' the effects of the alkyl sulfate chain length on mesomorphism, the chain length was varied for three different 3,4-dialkoxystilbazoles, namely the butyloxy, hexyloxy and dodecyloxy derivatives. Up to six different alkyl sulfates were used with $m=6$, 8, 10, 12, 14 and 16. The mesomorphism of the three series with $n=4$, 6 and 12, as a function of the alkyl sulfate carbon chain length, *m*, is shown in Fig. 4–6 respectively, the phase diagrams being drawn at the same scale. Thermal data are collected in Table 1.

A brief overview of the data shows that in general, the longer chain alkyl sulfates led to lower melting points, while longer chains on the stilbazoles led to stabilisation of the mesophases. Thus, there was a huge increase in the domains of stability of the mesophases with both increasing *m* and *n*. The mesophases were characterised by a combination of optical microscopy and X-ray diffraction. The cubic phases were seen as viscous, isotropic phases which could be observed growing as characteristic square features from either the columnar or isotropic phase. The columnar phases showed a characteristic fan-like texture which was indicative of a columnar hexagonal structure. The X-ray data for the columnar phases confirmed the assignment as hexagonal, and structural data are included in Table 2. X-Ray data were also consistent with the observation of a cubic phase, and allowed the phase to be identified as having $Ia\bar{3}d$ symmetry; some data are also included in Table 2. The detailed X-ray analysis will be published separately as part of a much larger structural study of related complexes.[9]

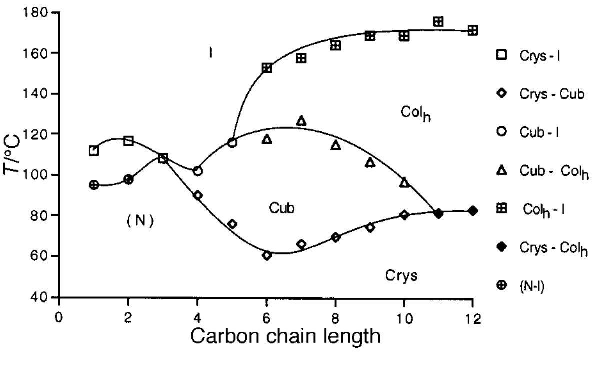


Fig. 3 Phase diagram for the complexes $[Ag\{St(n\text{-}3,4)\}_2][C_{12}H_{25}OSO_3]$

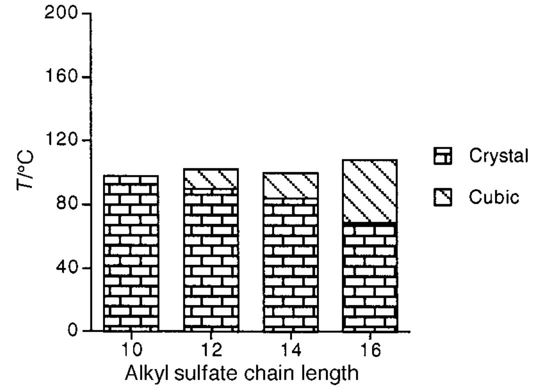


Fig. 4 Representation of the phase behaviour of $[Ag\{St(4\text{-}3,4)\}_2][C_mH_{2m+1}OSO_3]$

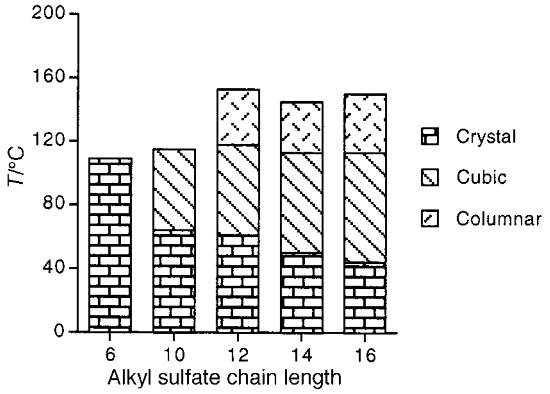


Fig. 5 Representation of the phase behaviour of $[Ag\{St(6\text{-}3,4)\}_2][C_mH_{2m+1}OSO_3]$

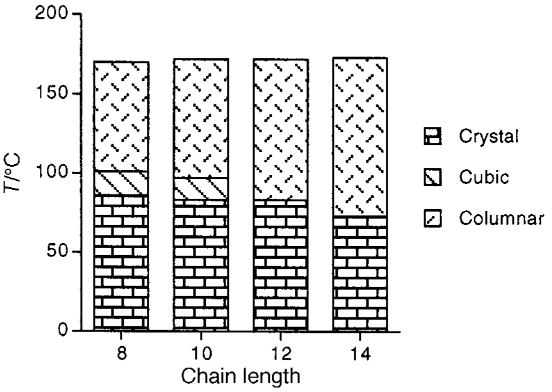


Fig. 6 Representation of the phase behaviour of $[Ag\{St(12\text{-}3,4)\}_2][C_mH_{2m+1}OSO_3]$

Table 1 Thermal behavior of the complexes

m	transition	T/ °C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
3,4-dibutyloxystilbazole				
10	Crys–I	98	29.0	78
12	Crys–Cub	90	27.9	77
	Cub–I	102	2.1	6
14	Crys–Cub	84	30.1	84
	Cub–I	102	1.0	3
16	Crys–Crys′	53	12.6	39
	Crys′–Cub	69	20.9	61
	Cub–I	108	1.0	3
3,4-dihexyloxystilbazole				
6	Crys–I	109	25.2	66
10	Crys–Cub	64	29.6	88
	Cub–I	115	2.6	7
12	Crys–Cub	61	29.3	88
	Cub–Col$_\mathrm{h}$	118	2.6	7
	Col$_\mathrm{h}$–I	153	1.0	2
14	Crys–Cub	50	46.7	144
	Cub–Col$_\mathrm{h}$	113	2.5	6
	Col$_\mathrm{h}$–I	145	0.4	1
16	Crys–Crys′	34	2.3	8
	Crys′–Cub	44	13.8	43
	Cub–Col$_\mathrm{h}$	113	2.0	5
	Col$_\mathrm{h}$–I	150	0.8	2
3,4-didodecyloxystilbazole				
8	Crys–Crys′	80	17.2	49
	Crys′–Crys″[a]	86	45.6	127
	Crys″–Col$_\mathrm{h}$	101	2.6	7
	Col$_\mathrm{h}$–I	170	—	—
10	Crys–Crys′	37	12.8	41
	Crys′–Crys″	62	10.4	31
	Crys″–Crys‴[a]	83	39.4	111
	Crys‴–Col$_\mathrm{h}$	97	2.6	7
	Col$_\mathrm{h}$–I	172	3.3	8
12	Crys–Crys′	71	54.8	159
	Crys′–Col$_\mathrm{h}$	83	10.6	30
	Col$_\mathrm{h}$–I	172	3.7	8
14	Crys–Crys′	60	18.9	57
	Crys′–Col$_\mathrm{h}$	73	91.5	275
	Col$_\mathrm{h}$–I	173	1.8	4

[a] The Crys″ phase ($m=8$) and the Crys‴ phase ($m=10$) are the isotropic crystal phases referred to in the text.

Table 2 Structural parameters for the columnar phase of the complexes

m	T/°C	phase	d_{211}/d_{01}[a]
3,4-dihexyloxystilbazole			
12	95	Cub	31.5
14	95	Cub	31.8
14	130	Col$_\mathrm{h}$	29.8
16	95	Cub	31.8
16	130	Col$_\mathrm{h}$	30.4
3,4-didodecyloxystilbazole			
8	130	Col$_\mathrm{h}$	35.5
10	130	Col$_\mathrm{h}$	35.3
12	130	Col$_\mathrm{h}$	35.7
14	130	Col$_\mathrm{h}$	35.8

[a] d_{211} for cubic phase; d_{10} for columnar phase.

The phase behaviour of the 3,4-dibutyloxystilbazole complexes as a function of the alkyl sulfate chain length (Fig. 4) showed that for $m=10$, the complex was non-mesomorphic, while for $m \geqslant 12$, a cubic phase was seen whose phase range increased from 12 °C ($m=12$) to 38 °C ($m=16$), due both to destabilisation of the crystal phase and stabilisation of the cubic phase. For the 3,4-dihexyloxystilbazole complexes (Fig. 5), it was found that for $m=6$, the complex was non-mesomorphic, while for $m=12$, 14 and 16, both a cubic and a columnar phase were observed while the complex with $m=10$ showed only a cubic phase. The mesomorphism of the 3,4-dodecyloxystilbazole complexes (Fig. 6) was dominated by the formation of a columnar hexagonal phase with a wide (≈ 100 °C) range for $m=12$ and 14, the often-observed cubic phase having completely disappeared. However, on heating the complexes with $m=8$ and 10, they first formed a phase which appeared optically isotropic and which gave many reflections in the X-ray diffraction pattern, suggesting a crystalline cubic phase. However, on annealing for some 20 min (*e.g.* at 100 °C for $m=10$), a birefringent texture was found to be growing in which resembled that of a columnar phase; the columnar phase subsequently cleared at a higher temperature. These observations will be discussed subsequently in a paper detailing the structural studies on these materials.

In general, the mesomorphism in 3,4-disubstituted polycatenar systems can be regarded as depending to a very large degree on the curvature at the aromatic/paraffinic interface,[10] by analogy with lyotropic systems for which the interfacial curvature is defined by the ratio between the volume of the lipophilic moiety and that of the hydrophilic moiety.[11] Thus, at short chain lengths, nematic and smectic C phases can be seen as there is little or no curvature at the interface, while at much longer chain lengths, a significant curvature is introduced which tends to promote the formation of columnar phases formed from repeating units apparently containing 3–4 molecules. In certain cases, the change from lamellar to columnar mesomorphism happens on moving from one homologue to the next,[12] although it is more common to see some homologues exhibiting, for example, both a smectic C and a columnar phase. However, it is also common to see that at some intermediate value of the curvature, a cubic phase is inserted into the phase sequence between the lamellar and columnar phase. This is beautifully illustrated by the phase diagram of some tetracatenar bipyridines.[13] The curvature therefore arises as a mismatch between the volume of the molecular core and that of the chains, and so in the silver complexes it is necessary to take into account the contributions of the rigid core, the chains and the anion. Against this background, we can then rationalise the mesomorphism of the complexes in this study. Transitions between phases in individual homologues are then generally accounted for by the increased volume of the chains which results from greater motion at higher temperature.

Our previous work with tetracatenar silver complexes with $m=12$ showed[8] that at shorter chain lengths, the cubic phase predominated, while our much earlier work with simple, two-chained, calamitic silver complexes showed that for cubic phases to be seen, longer stilbazole chain lengths were needed and the anion chain had to extend out beyond the rigid, aromatic core of the molecule, which happened only for $m \geqslant 12$. In this case, when the alkyl sulfate chain crosses the aromatic/paraffinic interface, it contributes to the increase in the curvature in such a way that a cubic phase is formed, although over a shorter temperature range than in the case of the tetracatenar silver complexes. In this two-chained system, the cubic phase can be seen as a frustrated structure, owing to the presence of a $\mathrm{S_A}$ phase above the cubic, and a $\mathrm{S_C}$ phase below it. However, when the alkyl sulfate is confined in the aromatic part of the molecule, there is no contribution to the curvature and as a result, only smectic and nematic phases are seen. These complexes behave as simple calamitic mesogens.

In the case of the 3,4-dibutyloxystilbazoles, when the anion extends beyond the core and as such contributes to chain volume and, to a lesser extent, the curvature, then a cubic phase appears whose stability increases with increasing alkyl sulfate chain length. However, neither the density of chains, nor the degree of curvature, is sufficient to stabilise a columnar phase. However, for $m=10$, the anion cannot contribute to the chain volume and the two butyloxy chains are too short to create the curvature (Fig. 7) necessary for the formation of a cubic phase, so no cubic phase is seen and the complex simply melts to isotropic on heating. Interestingly, it is also clear that what curvature is induced is sufficient to suppress the formation of lamellar or nematic phases.

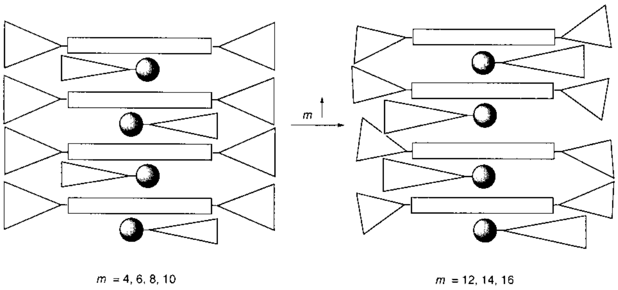


Fig. 7 Schematic diagram to show the relative steric effects of lateral alkyl sulfate chains

A similar explanation accounts for the lack of mesomorphism in the 3,4-dihexyloxystilbazole complexes with a hexyl sulfate anion, in that the stilbazole chains alone are insufficient to give rise to a curvature that stabilises the cubic phase in the absence of a contribution from the anion chain. However, the presence of the cubic and columnar phase for $m \geqslant 12$ is consistent with the general mesomorphism of tetracatenar materials. The slightly unexpected result is that for $m = 10$, a cubic phase is seen when the anion chain does not extend beyond the rigid, aromatic core and this is difficult to rationalise in the light of the absence of mesomorphism for the same stilbazole when $m = 6$, particularly as in this latter case, the core volume (including the anion) is smaller.

The mesomorphism of the 3,4-didodecyloxystilbazole complexes is entirely consistent with that now expected and the volume occupied by the ligand chains is the dominant parameter, giving rise to an interfacial curvature allowing stabilisation of the columnar phase only.

We can now begin to obtain some understanding of the general rôle of the intermolecular ionic interactions which we proposed previously[6] as being significant in stabilisation of the cubic phases in these compounds. Recall once more that in the simple two-chained silver complexes with alkyl sulfate anions, N, S_A, S_C and cubic phases are seen. However, in analogous, non-ionic complexes of palladium(II) (Fig. 8) which possess a lateral substituent, only nematic phases are seen and indeed, such behaviour is typical of mesogens substituted by lateral alkyl chains.[14]

That a nematic phase is seen at all in any of the silver complexes shows that the molecules can exist as discrete (ion-paired) entities, at least when the chain length is short. However, as the stilbazole chain length is increased, the resulting microphase separation tends to promote a layering. In the absence of ionic interactions, such microphase separation would not occur in a laterally alkylated system, but in these cases, the layering must be stabilised by the additional ionic interactions possible. Thus, the microphase separation and ionic interactions act synergically to stabilise lamellar phases, and the volume of the molten lateral chain cannot lead to the formation of a nematic phase, rather exerting a steric influence generating some degree of curvature at the aromatic/aliphatic interface. So long as the chain is confined within the extent of the rigid core the steric influence is clearly not large which implies that the ionic interactions are quite strong, but once the chain extends beyond the core (at $m = 12$), then its contribution to the interfacial curvature is greatly enhanced as it begins to 'interfere' with the terminal alkoxy chains. For two-chained systems, this additional curvature leads to the formation of cubic phases, while for tetracatenar systems, both cubic and columnar phases are observed. It may then be that in the case of the 3,4-dihexyloxystilbazole complexes of silver decyl sulfate where a cubic phase is rather unexpectedly observed, that ionic interactions are playing a key rôle is stabilising the cubic phase.

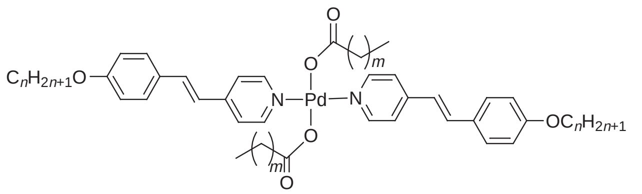


Fig. 8 Structure of laterally substituted palladium stilbazole complexes

One way of attempting to evaluate such an idea is to study extensively the mesomorphism of complexes of palladium carboxylates bearing polycatenar stilbazoles; these studies are currently underway and the results will be reported in due course.

Experimental

Dichloromethane was distilled from calcium hydride, methanol from magnesium and iodine, and acetone from potassium permanganate. Diethyl ether was dried and stored over sodium wire. All other chemicals were used as supplied. 3,4-Dialkoxystilbazoles were synthesised as described previously.[8]

Proton and carbon NMR spectra were recorded on a Brüker ACL250 spectrometer and referenced to external tetramethylsilane. In order to measure with accuracy the different coupling constants ($^2J_{HH}$, $^3J_{HH}$ and $^4J_{HH}$), a program Window NMR (1D-Win NMR, Brüker, MS Windows) was used. The assignment of all the carbon peaks was possible using one-bond ($^1J_{CH}$) and multiple-bond ($^2J_{CH}$, $^3J_{CH}$ and $^4J_{CH}$) C–H correlation[15] as well as the estimation of ^{13}C and ^{1}H chemical shifts in substituted benzenes.[16] Microanalysis was performed by the University of Sheffield micro-analytical service. The study of the thermal behaviour of the complexes was achieved by DSC analysis, carried out using a Perkin-Elmer DSC7 instrument using various heating rates (2, 5 and 10 K min^{-1}) and the mesomorphism was studied by hot-stage, polarising microscopy using a Zeiss Labpol microscope equipped with a Linkam TH600 hot-stage and PR600 temperature controller.

Sodium alkylsulfates

The procedure is illustrated for sodium decyl sulfate and follows a general method described by Gilbert.[17] All other alkyl sulfate salts were similarly prepared.

Chlorosulfonic acid (1.5 g, 12.6 mmol) was added dropwise to a flask containing diethyl ether (50 cm3), and the mixture was left stirred for a few min. Decan-1-ol (2 g, 12.6 mmol) in diethyl ether (20 cm^3) was then added to the solution, and the stirring was maintained for 30 min. The solvent was evaporated *in vacuo* and the residue was dissolved in ethanol (100 cm^3, 95% v/v). Sodium hydroxide (0.5 g, 12.6 mmol) was added, and the solution was stirred for 5 h. The precipitate was filtered, washed thoroughly with absolute ethanol, and then with diethyl ether. Sodium decyl sulfate was obtained in good yield (70%, 2.3 g) after being air-dried.

Silver(I) alkyl sulfates

The procedure is illustrated for silver decyl sulfate. Silver salts of longer-chain alkyl sulfates were similarly prepared, but the hexyl- and octyl-sulfate salt could not be so obtained as they were too soluble in water.

Sodium decyl sulfate (2.3 g, 8.8 mmol) in warm water (10 cm^3) was added to an aqueous solution of silver nitrate (1.5 g, 8.8 mmol) and the resulting mixture stirred for 2 h, in the vessel protected from light. The precipitate was filtered, washed with cold water and dried under high vacuum. The yield was 80% (2.4 g).

Bis[(3,4-dialkoxy)-4′-stilbazole]silver(I) alkyl sulfates

The complexes with an alkyl sulfate with more than 10 carbons were directly prepared as described below, while the hexyl- and octyl-sulfate complexes were obtained in two steps as described later.

A solution of 3,4-diheptoxy-4′-stilbazole (500 mg, 1.22 mmol) in dichloromethane (10 cm3) was added dropwise to a stirred suspension of $AgC_{12}H_{25}OSO_3$ (250 mg, 0.67 mmol) in dichloromethane (10 cm^3) and stirred (4 h, room temp.) with the vessel protected from the light. The mixture was then filtered through Celite and the solvent removed under reduced pressure. The yellow solid was crystallised from hot acetone and then recrystallised from methanol. The product was collected as a pale yellow solid in 67% yield (488 mg).

All the other complexes were similarly prepared and obtained in similar yields. The analytical data are collected in Table 3; ^1H and ^{13}C NMR data are given below.

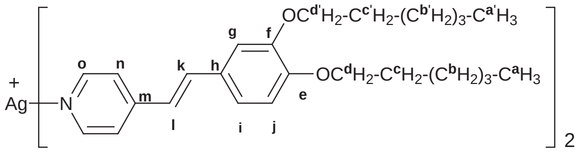
Typical preparation of the hexyl- and octyl-sulfate silver(I) complexes

The preparation of these complexes involved the formation of the triflate complex followed by a metathesis reaction with the relevant sodium alkyl sulfate.

3′,4′-Didodecyloxy-4-stilbazole (250 mg, 4.6×10^{-4} mol) was stirred in acetone (5 cm^3) with silver trifluoromethanesulfonate (60 mg, 2.3×10^{-4} mol) at room temperature in the dark for 4 h. The mixture was then cooled in ice and the precipitate formed was filtered and washed with cold acetone to yield the pure complex (94%, 291 mg) as a pale yellow solid of analytical purity.

A solution of the complex previously prepared (150 mg, 1.1×10^{-4} mol) in acetone (20 cm^3) was added to stirred suspension of sodium octyl sulfate (77 mg, 3.3×10^{-4} mol) in the same solvent (10 cm^3) and was heated at reflux in the dark for 12 h. When cooled, the solution was filtered through Celite, to eliminate the excess of sodium octyl sulfate, and the solvent evaporated. The solid was then crystallised once from methanol, and twice from acetone. The complex was recovered by filtration, washed with acetone and dried under vacuum. Yield 65% (102 mg).

$[Ag\{St(6\text{-}3,4)\}_2][GoH_{21}OSO_3]$ Spectroscopic data



$C^sH_3\text{-}(C^rH_2)_7\text{-}C^qH_2\text{-}C^pH_2\text{-}OSO_3^-$

The ^1H and ^{13}C NMR data for $[Ag\{St(6\text{-}3,4)\}_2]$-$[C_{10}H_{21}OSO_3]$ are given in detail. The spectra for all other complexes were effectively identical save for the number of protons/carbons associated with the various alkyl chains.

δ_H(250.13 MHz, $CDCl_3$): 0.85 (**s**, t, $^3J = 6.7$ Hz, 3 H), 0.89 (**a**, **a**′, t, $^3J = 6.6$ Hz, 12 H), 1.38 (**b**, **b**′, **r**, m, 38 H), 1.54 (**q**, m, 2 H), 1.80 (**c**, **c**′, m, 8 H), 3.95, 3.98 (**d**, **d**′, 2 t, $^3J = 6.6$ Hz, 8 H), 4.16 (**p**, t, $^3J = 6.7$ Hz, 2 H), 6.66 (**l**, AB, $^3J_{lk} = 16.6$ Hz, 2 H), 6.70 (**j**, d, $^3J_{ji} = 7.9$ Hz, 2 H), 6.86 (**i**, dd, $^4J_{ig} = 2.0$ Hz, $^3J_{ij} = 7.9$ Hz, 2 H), 6.95 (**g**, d, $^4J_{gi} = 2.0$ Hz, 2 H), 7.17 (**k**, AB, $^3J_{kl} = 16.6$ Hz, 2 H), 7.26 (**n**, AA′XX′, $|J_{no} + J_{no'}| = 6.5$ Hz, 4 H), 8.68 (**o**, AA′XX′, $|J_{on} + J_{on'}| = 6.5$ Hz, 4 H). δ_C(62.9 MHz, $CDCl_3$): 13.8 (**a**, **a**′), 14.1 (**s**), 22.6, 25.3, 26.0 29.1, 29.2, 29.4, 29.7, 31.4, 31.6 (**b**, **b**′, **c**, **c**′, **r**), 32.0 (**q**), 67.9 (**p**), 69.2, 69.4 (**d**, **d**′), 111.8 (**g**), 113.0 (**j**), 121.4 (**n**), 121.5 (**i**), 122.3 (**l**), 128.2 (**h**), 135.6 (**k**), 147.2 (**m**), 149.2 (**e**), 150.7 (**f**), 152.2 (**o**).

Table 3 Analytical data for the complexes

		found (calc.) (%)							
m	yield (90)	C		H		N		S	
3,4-dibutyloxystilbazole									
10	76	62.3	(62.7)	7.5	(7.6)	3.2	(2.8)	3.6	(3.2)
12	78	63.0	(63.3)	7.5	(7.8)	2.5	(2.7)	3.0	(3.1)
14	67	63.6	(63.9)	7.8	(7.9)	2.6	(2.7)	2.9	(3.0)
16	30	63.9	(64.5)	8.0	(8.1)	2.6	(2.6)	3.1	(3.0)
3,4-dihexyloxystilbazole									
6	58	63.0	(63.9)	8.0	(7.9)	2.7	(2.7)	3.5	(3.0)
10	52	64.7	(65.0)	8.3	(8.3)	2.8	(2.5)	2.8	(2.9)
12	78	65.3	(65.5)	8.1	(8.4)	2.5	(2.5)	3.0	(2.8)
14	61	65.8	(66.0)	8.6	(8.6)	2.5	(2.4)	2.6	(2.7)
16	56	66.6	(66.5)	8.7	(8.7)	2.4	(2.3)	2.5	(2.7)
3,4-didodecyloxystilbazole									
8	65	68.8	(69.4)	9.3	(9.6)	2.4	(2.0)	2.6	(2.3)
10	74	69.2	(69.8)	9.8	(9.7)	2.1	(1.9)	2.2	(2.2)
12	83	69.7	(70.1)	9.6	(9.8)	1.8	(1.9)	2.3	(2.2)
14	62	70.5	(70.4)	9.8	(9.9)	1.9	(1.9)	2.3	(2.1)

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