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SOLVENT-INDUCED MESOMORPHISM IN CALAMITIC COMPLEXES OF SILVER(I)

ИНДУЦИРОВАННЫЙ РАСТВОРИТЕЛЕМ МЕЗОМОРФИЗМ В КАЛАМИТНЫХ КОМПЛЕКСАХ С СЕРЕБРОМ(I)

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Calamitic stilbazole complexes of silver(I) containing a tetradecylsulfate anion have been studied. The thermotropic behaviour of these materials shows the presence of nematic, SmC, SmA, S_4 *and cubic phases. On addition of solvent, three types of behaviour can be discerned: apolar solvents associate with the ligand terminal chains and promote phases with curved interfaces; small dipolar, aprotic solvents associate with the core and favour mesophases that do not possess curved interfaces, while short-chain alcohols hydrogen bond with the ionic core of the complexes to form ribbon-like structures that organise into chromonic phases. This solvent-induced behaviour is compared with the solvent-induced behaviour of analogous polycatenar complexes of silver(I) and with more conventional, calamitic organic compounds with hydroxy-terminated chains.*

***Key words**: calamitic mesogens, metallomesogens, solvent-induced mesomorphism, silver.*

Исследованы каламитные комплексы алкоксистильбазола с серебром(I), содержащие тетрадецилсульфатный анион. Термотропный мезоморфизм этих материалов характеризуется наличием нематической, SmC, SmA, S_4 *и кубической фаз. При добавлении растворителя распознаются три типа поведения: аполярные растворители ассоциируются с терминальными заместителями лиганда и стимулируют формирование мезофаз с искривленными поверхностями; маленькие диполярные апротонные растворители ассоциируются с ядром и благоприятствуют мезофазам, которые не обладают искривленными поверхностями; низшие спирты формируют водородные связи с ионным ядром комплексов с образованием лентообразных структур, которые организуются в хромонические фазы. Подобное поведение, индуцированное растворителем, сравнивается с аналогичным поведением поликатенарных комплексов серебра(I), а также с традиционными каламитными органическими соединениями, имеющими в качестве терминальных заместителей гидроксильные группы.*

***Ключевые слова:** каламитные мезогены, металломезогены, индуцированный растворителем мезоморфизм, серебро.*

Introduction

Alkoxystilbazole complexes of silver(I) (fig. 1) are quite remarkable materials. This group has studied them extensively over several years and the following properties have been

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reported: the formation of nematic phases in formally ionic materials [1]; the observation of smectic phases in complexes with lateral flexible chains [2]; an extensive series of materials with cubic phases [3]; a large family of polycatenar mesogens [4] in which the molecular core is very much shorter than that found normally in polycatenar systems [5]. As a result of these studies, captured in critical review articles [6], and related studies of palladium(II) and platinum(II) analogues [7], significant progress in the understanding of the formation of thermotropic cubic phases and of the lamellar-to-columnar 'transition' in polycatenar systems. A common factor underlying several of these observations is the presence, at the centre of the molecule, of the silver ion, which is in close association with the attendant anion. Thus, for example, it is intermolecular ionic interactions of this fragment that are held responsible for the observation of lamellar phases (SmC and SmA) where the anion is the flexible, long-chain dodecylsulfate [8].

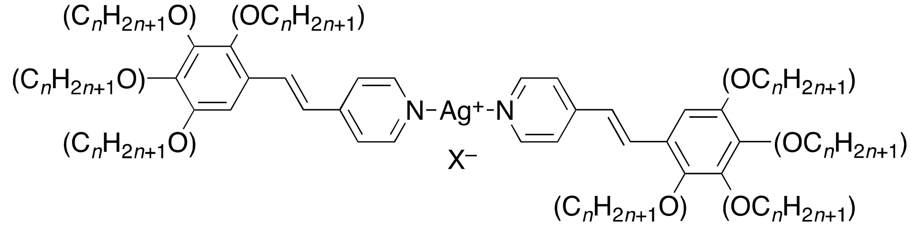


Fig. 1. The common molecular structure of polycatenar silver(I) alkoxystilbazole complexes **1** (X = CF_3SO_3, $C_mH_{2m+1}OSO_3$)

More recently, we undertook a study of the effect of solvent on the mesomorphism of polycatenar derivatives of these complexes (fig. 1: **1**) [9]. Thus, it is known from the study of thermotropic polycatenar materials that the change in mesomorphism from lamellar to columnar, in some cases through the intermediacy of a cubic phase, is driven by the different volumes of the rigid core of the molecules and that of the terminal chains. Thus, as the volume of the chains increases, mesophases with curved structures are preferred (cubic, columnar) in order to fill space efficiently [10]. In studying the effect of added solvents on the polycatenar silver(I) complexes, two types of behaviour were seen, so that in one case, small polar alcohols clearly associated strongly with the ionic core of the complex to give what are believed to by hydrogen-bonded ribbons leading to so-called chromonic behaviour and the observation of, for example, nematic and tetragonal (S_4-phase analogues) phases. In other cases, it was found that apolar solvents such as alkanes gave an effect equivalent to adding terminal alkyl chain volume (promoting phases with curvature), whereas small, polar, aprotic solvents clearly associated with the polar core and had the opposite effect, destabilising phases with curvature. Such behaviour is entirely consistent with the concepts of 'internal solvent' and 'external solvent' advanced by Usol'tseva and Praefcke in their work with solvent-induced mesomorphism of large, discotic complexes of palladium(II) and platinum(II) [11].

Having studied these polycatenar systems extensively, it was then of some interest to address the possible solvent-induced mesomorphism of calamitic silver(I) complexes, especially given the paucity of literature reports of such behaviour in calamitic materials in general. Thus, in a series of papers, Tschierske and co-workers [12, 13, 14] had studied families of compounds, examples of whose general structure is represented in Figure 2. While several examples were non-mesomorphic, many anhydrous materials formed SmA phases with both SmC and SmB phases seen alongside some crystal G and K phases. The preponderance of lamellar phases is readily understood by the presence of alcohol groups at the chain termini. Added water was taken up in the layer interface regions where it could interact with the alcohol functions and so modified the mesomorphism.

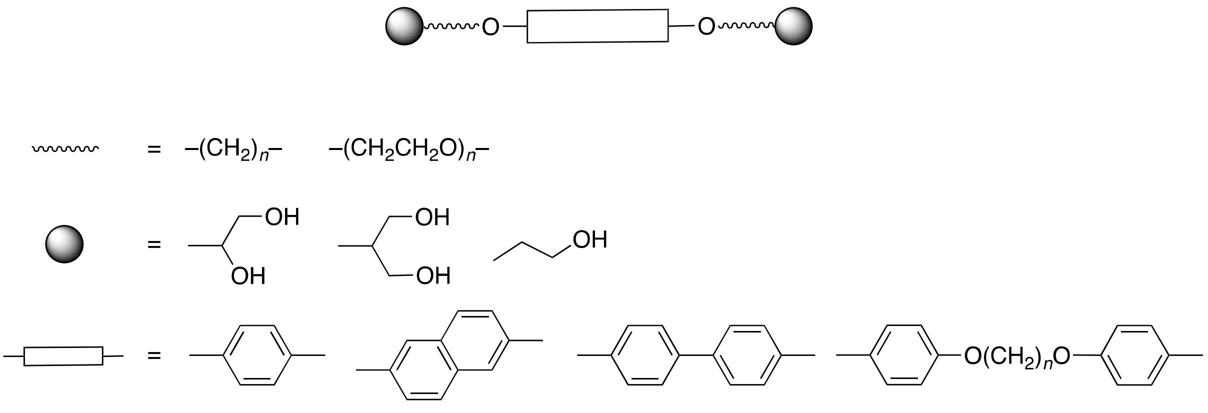
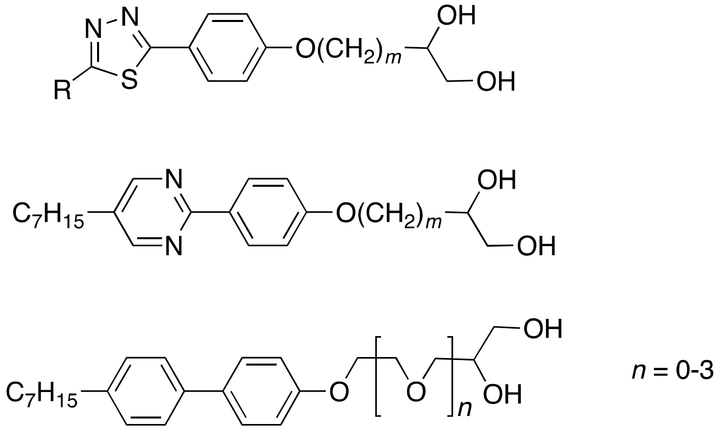


Fig. 2. Examples of the general structure of the complexes studied by Tschierske and co-workers [12, 13, 14]

Specific examples that illustrate the way in which added solvents modified the mesomorphism are shown in fig. 3. Thus, on addition of water, the SmA phase of **(a)** was stabilised significantly while its SmC phase was destabilised [12], whereas **(b)** was non-mesomorphic as an anhydrous compound yet both SmA and SmC phases were induced when water was added [13]. For compound **(c)** [14], it was found also that solvents such as ethylene glycol and formamide were able to influence the mesomorphism and, for example, addition of the former solvent suppressed the SmC phase of the anhydrous material and destabilised the SmA phase.


(a)

(b)

(c)

Fig. 3. Specific examples of compounds with mesomorphism modified by the addition of solvent

An important conclusion of this work was that on addition of solvent to these anhydrous materials, the phases that formed were not truly lyotropic and it was further observed that no phases with curved interfaces (hexagonal, cubic) were observed. Further, the authors found that water uptake was limited and that when saturation was reached, an excess of water could be observed. In our studies of solvent-induced mesomorphism of polycatenar silver(I) complexes, we made identical observations; however, we went further by constructing a binary phase diagram for one silver complex with DMSO. In that phase diagram, we observed that after the uptake of a certain amount of DMSO, biphasic behaviour was seen and we were able to calculate that the critical amount taken up was equivalent to *ca* 2 molecules of DMSO per cation/anion pair. Thus we proposed that in these systems, it certainly was not a lyotropic phase that was under observation, rather the thermotropic phase of a solvate and this interpretation is consistent with the observations of Tschierske and co-workers [12 – 14].

Results

The general structure of the materials is shown in fig. 4 and the complexes chosen for this study are tetradecylsulfate salts (X = $C_{14}H_{29}OSO_3$) with $n = 5$ (**2a**) and $n = 8$ (**2b**).

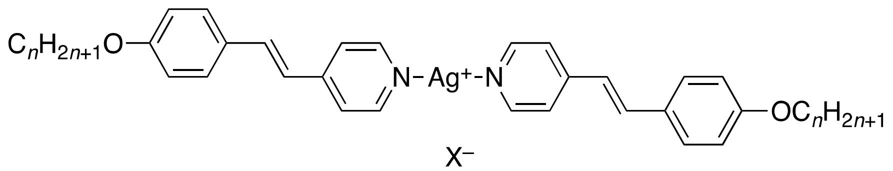


Fig. 4. General structure of the calamitic bis(4-alkoxystilbazole)silver(I) complexes, **2** (X = CF_3SO_3, $C_mH_{2m+1}OSO_3$, BF_4, NO_3)

As suggested in the introduction, the mesomorphism of these calamitic materials is fascinating in that as ionic compounds they form nematic and SmC phases and many examples show a cubic phase, identified as having *Ia*3*d* symmetry where X = $C_{12}H_{25}OSO_3$ and $6 \leq n \leq 12$ [3]. The formation of the cubic phase was found to be a delicate function of the terminal chain length (n) and the alkylsulfate chain length (m), so that for $m = 8$, 10 no cubic phases were seen, whereas for $m \geq 12$, cubic phases were seen typically for $n \geq 6$. Thus, a crucial factor was the observation that cubic phases formed only when the anion chain extended beyond the rigid stilbazole core ($m = 12$).

Table 1

Mesomorphism of calamitic complexes 2 (based on DSC data)

Compound	Transition	T / °C[b]	ΔH / kJ mol^{-1}	ΔS / J K^{-1} mol^{-1}
2a AgTES5-4	Cr – SmA	146,0	34,4	82
	SmA – N	167,5	0,9	2
	N – Iso[a]	169	–	–
	(SmA – SmC)	(132,5)	(1,2)	(3)
2b AgTES8-4	Cr – Cub	133,3	25,0	62
	Cub – SmA	156,8	2,7	6
	SmA – Iso	161,6	0,7	2
	(SmA – S_4)	(147,0)	(0,1)	(0,1)
	(S_4 – Cub)	(143,5)	(2,9)	(7)

[a] No peak on DSC, data taken from polarising microscopy.

[b] Data taken from 2nd heating (for enantiotropic phases) and 1st cooling (for monotropic phases)

Of the materials selected for study, the shorter homologue **2a** showed SmA and nematic phases with, in addition, a SmC phase that is seen monotropically (table 1). The longer-chain homologue **2b** displays Cub and SmA phases on heating, while on cooling the transition from SmA to Cub occurs through the intermediary of a birefringent S_4 phase with mosaic texture (table 1, fig. 5). The S_4 phase usually appears in conjunction with cubic phase and, based on X-ray analysis, it was suggested that the phase could have a three-dimensional tetragonal structure with $I4_1/acd$ space group. [15] The mesomorphism of these complexes is summarised in table 1.

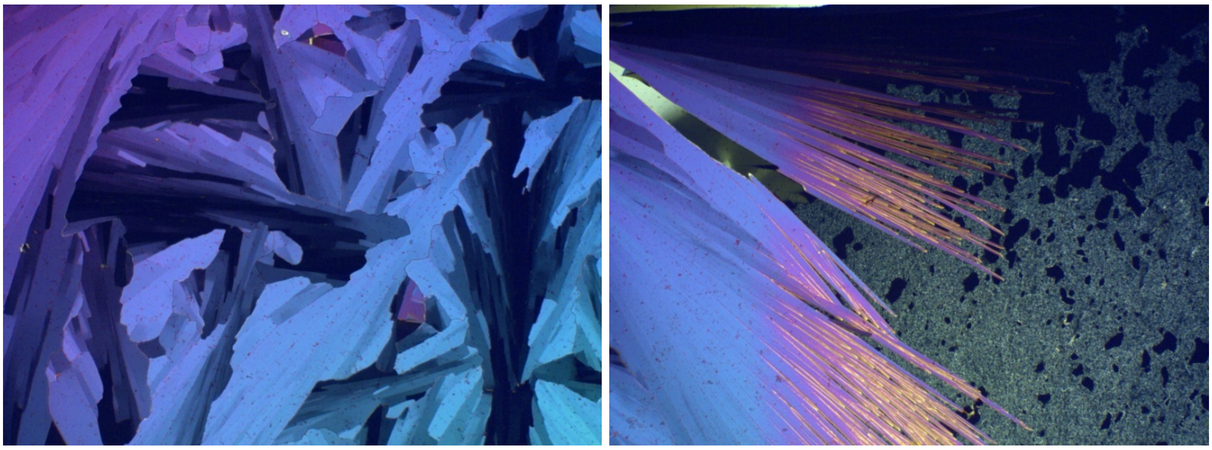

a *b*

Fig. 5. *a* – Texture of thermotropic S_4 phase of compound **2b** at 145 °C;
b – growth of thermotropic S_4 phase (on left) on cooling from SmA phase of compound **2b** at 145 °C

Mixtures with DMF and DMSO

Earlier, we described the use of small, polar, aprotic solvents (MeCN, DMF and DMSO) for induction of mesomorphism in mixtures with polycatenar alkoxystilbazole complexes and we assumed that these solvents were incorporated towards the polar core of the complexes, thereby reducing the interfacial curvature [9]. In the present work, acetonitrile could not be used as its low boiling point (80 – 82 °C) causes it to evaporate before any melting transition occurs. DMF and DMSO are higher boiling solvents (T_{bpt} = 153 and 189 °C, respectively) and were used without problem.

Thus, in contact preparations with DMF and DMSO, complex **2a** showed an induced S_4 phase, although it appeared only monotropically. This phase was observed on cooling from the SmC phase and existed up to beginning of crystallisation, observed between 113 – 105 °C and 116 – 104 °C with DMF and DMSO, respectively. Yet despite the induction of an S_4-like phase, no induction of a cubic phase was observed for **2a** with DMF or DMSO.

A monotropic S_4 phase was observed in solvent-free **2b** but on cooling from the SmA phase. Contact preparations of **2b** with DMF showed that this solvent destroys thermotropic cubic phase, at the same time broadening the SmA phase range (fig. 6). For example, in contact preparations of **2b** with DMF the SmA phase was found between 112 and 167 °C on heating, while solvent-free complex displays this phase between 155 and 167 °C.

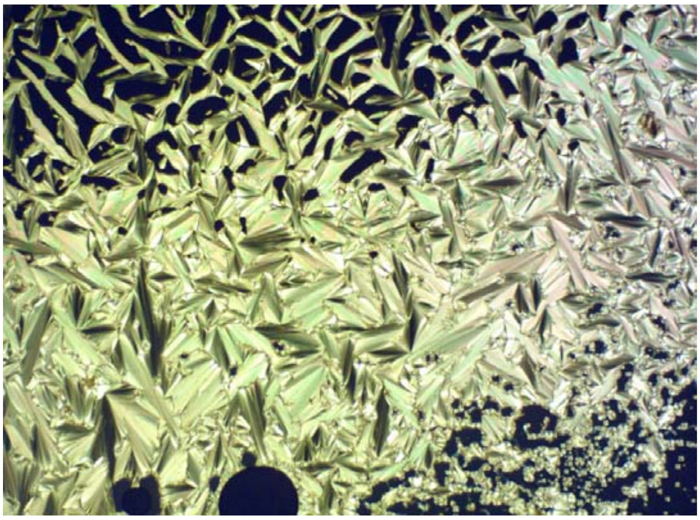


Fig. 6. Texture of SmA phase in mixture of complex **2b** with DMF at 119 °C, on cooling. The smectic phase appears from isotropic in the form of bâtonets

Mixtures with alcohols

For polycatenar alkoxystilbazole complexes reported previously, it was found that alcohols were 'special' solvents. Thus, there was a difference in the effect of alcohols depending on the extend of their aliphatic part so that the lower alcohols (methanol, ethanol and propanol) allowed induction of a nematic phase, which is believed to have a chromonic-like character [16] due to possible H-bonding between complexes and alcohols.

As complex **2a** has a thermotropic nematic phase as a solvent-free compound, any observation of a nematic phase would require careful interpretation and, in any case, the shorter-chain alcohols were too volatile to survive the melting temperatures of the complexes. Nevertheless, for complex **2b** a nematic phase was observed in a contact preparation with propanol (*ca* 109 °C), but it formed and disappeared rapidly as the solvent quickly evaporated. Interestingly, no nematic phase was observed in mixtures of **2b** with butanol. This latter observation is important, because it suggests that with propanol, once more it is a chromonic-type behaviour that is found and that this cannot happen with butanol, which most probably associated with a different part of the complex. Such a result and supposition are entirely consistent with our previous observations.

The higher alcohols (butanol-hexadecanol) have longer aliphatic chains that should contribute to hydrophobic part of supramolecular aggregate. This is clearly the case here as in contact preparations with pentanol and undecanol, complex **2a** showed induced monotropic S_4 and cubic phases, entirely consistent with them contributing to the chain volume. Mixing complex **2b** with the same alcohols showed that no new mesophases were induced.

Mixtures with hydrocarbons

From the work of Usol'tseva and Praefcke [11] and from our own studies [9], we know that hydrocarbons tend to associate with the apolar periphery of mesogens, as from compatibility principle, hydrophobic periphery is the only place where hydrocarbons can be incorporated, increasing the volume of these regions and acting in a manner equivalent to the addition of more/longer terminal chains.

Contact preparations of **2a** with both decane and tetradecane showed induction of a cubic phase (fig. 7, *a*) and a birefringent phase with a mosaic texture (fig. 7, *b*). From this texture alone it is not readily possible to assign this phase, but we note that several silver complexes of this type show a crystal G phase [3] and, while there is no evidence of any decomposition, that the free ligands show a crystal E phase [17]. Both induced phases were observed on cooling in the temperature range 100 – 70 and 105 – 89 °C with decane and tetradecane, respectively.

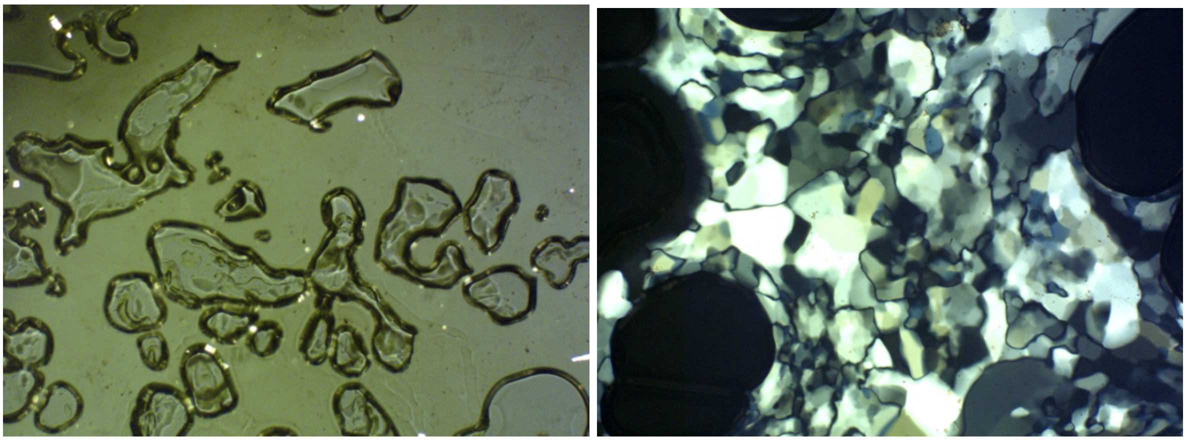


Fig. 7. Induced mesophases observed in different parts of contact preparation of complex **2a** with tetradecane on heating, 112 °C: *a* – cubic phase; *b* – unidentified ordered mesophase (see text)

In contact preparations of **2b** with the same aliphatic hydrocarbons, no new mesophases were induced. Thus, added solvents simply decreased the melting point drastically so that in the contact preparation **2b**/decane, the Cr → Cub transition was observed at 102 °C (down from 133 °C) and the cubic phase simply cleared directly to isotropic, showing a total suppression of the SmA.

Discussion

The above results show quite clearly that these calamitic materials behave in a manner identical to the related polycatenar complexes reported earlier, in that small, polar aprotic solvents associate with the polar core of the complexes to increase the effective volume of the core. Thus, addition of DMSO or DMF to complex **2b** leads to the destabilisation of its cubic phase and increases the range of the SmA phase. Similarly and by analogy, addition of decane or tetradecane to **2a** would be expected to lead to an effective increase in volume of the apolar chains, and it is apparent that this is so as a cubic phase is induced.

Longer-chain alcohols clearly behave as apolar solvents as is shown by the induction of a cubic phase in complex **2a**, while the shorter-chain propanol shows the induction of chromonic-type behaviour with the observation of a nematic phase in complex **2b**.

The fact that the solvent-induced behaviour of these two complexes shows a parallel with the behaviour of the analogous polycatenar systems reveals a pleasing degree of consistency, but also points to the very highly amphiphilic nature of these complexes. Thus, it is absolutely clear that there is a good segregation between the apolar and the polar parts of the complexes, for without this, the rather specific behaviour of the added solvents would not be possible. Of course, the literature of liquid crystals does use the language of 'microsegregation' to account for, for example, the prevalence of smectic over nematic phases as chain lengths increase. Nonetheless, it is tempting here to think that these silver complexes show a somewhat amplified amphiphilicity on account of the extremely polar nature of the core of the complex due to the presence of the ionic function. It remains to be seen if such an assertion is borne out by further experimental work.

Experimental

The complexes were prepared as described previously and their mesomorphism checked against previous data [18].

The solvents employed in this study: linear alkanes, small polar aprotic solvents (DMF and DMSO) and alcohols were used from suppliers as received. Solvent-induced mesomorphism was studied by polarising optical microscopy using the Lawrence penetration method. Thus, the sample and the solvent are mixed on the slide in such a way that a concentration gradient is established giving a snapshot of the binary phase diagram. Mesophases were identified by their characteristic optical texture and (for the cubic phase) viscosity. We should stress that this experimental procedure gives only a qualitative picture of the phase behaviour, it is not possible to determine exact temperature/concentration regions.

Conclusion

Calamitic stilbazole complexes of silver(I) with a tetradecylsulfate anion show solvent-induced modifications to their liquid crystal behaviour. The changes in behaviour are entirely consistent with consideration of the complexes as amphiphilic, so that apolar solvents associate preferentially with the terminal chains leading to the observations of mesophases that show increased curvature, while polar, aprotic solvents associate preferentially with the complex core favouring phases with linear interfaces. Chromonic behaviour is found with short-chain alcohols.

Acknowledgements

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