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Lyotropic mesomorphism in some thermotropic, polycatenar complexes of silver(I)

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A wide range of mesophases are induced on treating polycatenar complexes of silver(I) with a wide range of organic solvents.

Liquid crystal behaviour can be induced either by using temperature to effect changes between the solid, liquid and liquid crystal states (*thermotropic* mesogens), or by the action of solvent where the phase diagram evolves as a product of the concentration of the mesogenic species in that solvent (*lyotropic* mesogens).

By far the majority of materials which form lyotropic mesophases are surfactant amphiphiles such as long-chain ammonium compounds, and many of the mesophases consist of ordered arrays of micelles. Lyotropic mesophases are also formed of disk-like materials ('chromonic' phases),[1] and of polymeric materials such as group 10 metal acetylides[2] and DNA.[3] For DNA and for phases of discotic systems, mesomorphism is dominated by the formation of nematic and hexagonal phases and, in the case of the disk-like systems, it is columns of disks which organise to form these phases. A characteristic of lyotropic polymeric and disk-like systems is that they are not surface active and do not possess a critical micelle concentration.

While most compounds are either thermotropic or lyotropic, those that are both are termed *amphotropic*, and examples are known for rod-like and disk-like thermotropic mesogens as well as certain amphiphilic materials.[4]

For some time, we have been interested in the mesomorphism of thermotropic, polycatenar ('many-chained') mesogens[5] as for certain types, it is possible for the mesomorphism to change from that characteristic of rod-like mesogens to that of disk-like systems as a function of chain length. In particular, we have concentrated our studies on poly(alkoxy)stilbazole complexes of palladium(II), platinum(II)[6] and, more especially, silver(I).[7] In polycatenar systems, the phase behaviour is to a large degree dominated by the often conflicting spatial requirements of the molecular core and the chains attached to it. When this conflict is small lamellar phases result, but when it is great, the lamellae can break up giving cubic and columnar phases.[8] Clearly, in these systems the mesomorphism is a delicate function of the so-called *internal solvent*[9] (*i.e.* the chains) and so it might be expected that addition of *external* solvent would have a profound effect. Yet to date, this behaviour has not been studied in polycatenar systems. We have, therefore, begun a study of the lyotropic behaviour of our mesomorphic silver complexes and we now report on our initial findings.

The complexes which are the subject of this communication are shown in the Chart 1 and are typical examples of the materials we have studied. Our experience to date shows that there are four main classes of solvent which will induce lyotropic mesophases in these systems, namely alcohols, alkanes, cyclic hydrocarbons and small, polar, aprotic solvents. The experiments were of the Lawrence penetration type where 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. The examples chosen reflect the range of behaviour we observed and also identify the questions which arise from these experiments.

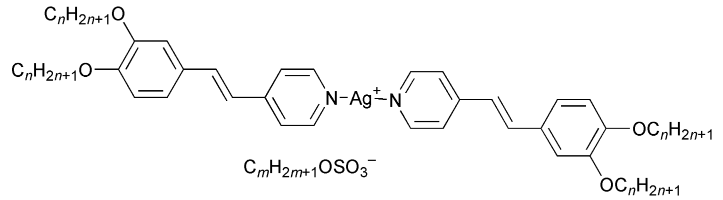
Compound **1** is non-mesomorphic (Cr·98·I) as a thermotropic mesogen,[10] but mixing with small polar solvents such as DMF and DMSO induces the formation of a lamellar phase, while longer-chain alcohols (propan-1-ol to undecan-1-ol) result in the induction of a monotropic cubic phase. However, methanol and ethanol are different, the former inducing formation of a nematic phase, while the latter induces nematic and lamellar phases. In addition, a highly birefringent monotropic phase is found which is extremely similar in texture to the so-called S_4 phase which is often found in association with the cubic phase of simple, calamitic mesogens and which has been shown to possess tetragonal symmetry.[11] Therefore, we make a preliminary assignment of this phase as tetragonal here, too.

When **1** is examined in apolar solvents, a monotropic cubic phase is induced in heptane, decane, pentadecane, benzene, cyclohexane, cyclohexene and tetraline.

We next turned our attention to **2** and **3** which possess a longer-chain anion than **1**. As a thermotropic material,[10] **2** posseses a cubic phase (Cr·84·Cub·102·I), while **3** shows both cubic and Col_h phases (Cr·50·Cub·113·Col_h·145·I).[10] Using small, dipolar aprotic solvents (MeCN, DMF, DMSO) each material showed a lamellar phase in addition to its thermotropic phases, but in common with **1**, the greatest degree of phase induction was found with short-chain alcohols. Thus, methanol induced a nematic, lamellar and tetragonal phase, while nematic and tetragonal phases were induced by ethanol and, for **2**, by propanol and butanol. A (columnar) hexagonal phase was also induced for **2** by alcohols from pentanol to undecanol.

To probe this behaviour further, we have begun to construct binary phase diagrams and that derived from **3** in DMSO is reproduced in Fig. 1. Samples were prepared by weighing out the requisite amounts of the two components, sealing them between two microscope slides and then allowing mixing to occur. Phase identification is by polarising optical microscopy.

The phase diagram shows first of all that the thermotropic columnar phase is strongly destabilised by the solvent and



1: $m = 10$, $n = 4$
2: $m = 14$; $n = 4$
3: $m = 14$; $n = 6$

Chart 1 Complexes used in this study.

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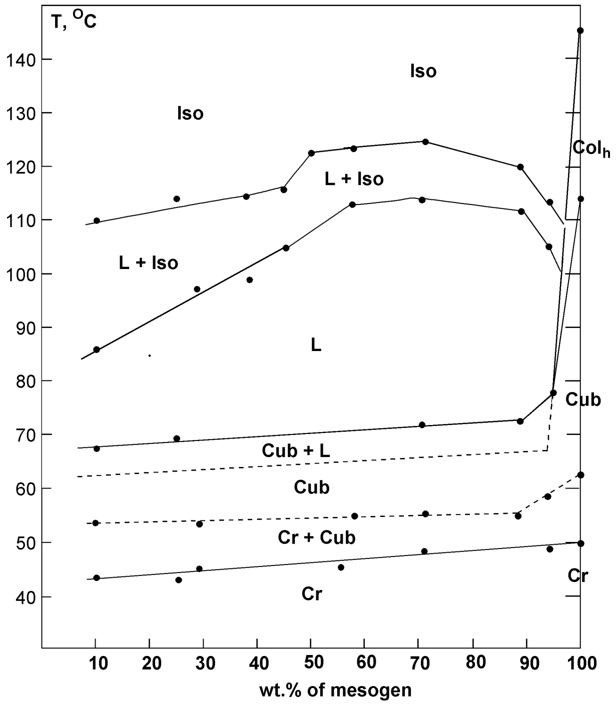

Fig. 1 Binary phase diagram for **3** with DMSO.

disappears in the presence of about 10 wt% of DMSO. The cubic phase is also strongly destabilised and whereas it clears to the Col$_h$ phase at 113 °C as a pure, thermotropic material, it does not exist above about 70 °C in the two-component system. From 10–90% solvent, the form of the phase diagram is approximately constant and shows, with increasing temperature, crystal, cubic, lamellar and isotropic phases, always separated by biphasic regions. Further, it seems that there is a maximum amount of solvent which is tolerated by the system, for at solvent concentrations greater than 30 wt%, free solvent is seen in addition to the mesophase.

All of these results require explanation and imply some fundamental questions. First, the polar nature of the core of these materials would account for the fact that there is solubility in dipolar aprotic solvents and also in the alcohols used, while the lipophilic exterior is consistent with solubility in alkanes and cyclic hydrocarbons. In considering the mesomorphism of polycatenar mesogens, the two main factors which are important relate to the area of the 'rigid' core at the core/chain interface and the volume occupied by the terminal chains. As the latter becomes greater with respect to the former, then there is a move from lamellar to columnar phases, often through some intermediate phase. The mesomorphism of polycatenar materials depends strongly on the number and length of the chains (internal solvent), and so the fact that the mesomorphism is influenced profoundly by the solvents used is consistent with the complementary idea of 'external' solvent.[9] Simplistically, we might imagine the small, polar solvent molecules associating with the polar core, while the hydrocarbon solvents would associate more with the ligand alkoxy chains. Thus, in the former case we might expect an increase in the effective core dimensions promoting a move from columnar to lamellar phases, while for alkane solvents, the effective chain volume should increase and promote a move from lamellar to columnar phases. The data we have given for the induction of new phases in complexes with existing thermotropic mesomorphism are consistent with these ideas. Further, we observe that where short-chain alcohols are used, nematic phases are often induced which we take as an indication of a rather strong interaction with the ionic core of the complexes, disrupting layer formation.

However, there is a more fundamental aspect of this work which needs to be addressed and which distinguishes these materials from other amphotropic materials. This relates to the nature of the species giving rise to the mesomorphism.

For example, amphiphiles form micelles and it is the ordering of these micelles at high concentrations which gives rise to the lyotropic mesophase. If we now turn our attention to polymeric systems, the situation is simple and it is the polymeric 'rod' itself which is the mesogen. In the case of columnar systems, the situation is similarly clear and we can consider the formation of columns of molecules which act as the mesogenic moiety, leading to nematic or hexagonal phases in a behaviour similar to that shown by polymeric materials. With these polycatenar systems, the situation is a little different. Thus we might consider that the columnar and cubic phases are similar in composition in both thermotropic and lyotropic cases, but the question arises as to the comparability of the dimensions and the extent to which the systems may simply be swollen. However, the species giving rise to the lamellar and, particularly, the nematic phase, is much less obvious. Part of the answer to these questions will come from structural parameters obtained from X-ray methods.

It is also of relevance here to compare these systems with recent work on rigid, aromatic amphiphiles[12] which were typically contituted by a biphenyl unit terminating in a diol function. These are not 'classical' lyotropic systems and were described as showing 'thermotropic mesomorphism of solvent complexes', the materials being saturated with solvent at 50 mol%, corresponding to around 5 wt%. While these silver systems do saturate, it is at much higher concentrations and the form of the phase diagram which we find is much more akin to a so-called 'chromonic' system than a solvent complex.

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Notes and references

1 N. V. Usol'tseva and V. V. Bykova, *Mol. Cryst., Liq. Cryst.*, 1992, **215**, 89 and references therein; J. E. Lydon in *Handbook of Liquid Crystals*, ed D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, vol. 2A, ch. XVIII, 1998.
2 *E.g.* S. Takahashi, Y. Takai, H. Morimoto and K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, 1984, 3.
3 F. Livolant and A. Leforestier, *Prog. Polym. Sci.*, 1996, **21**, 1115.
4 See *e.g.* A. Skoulios and V. Luzzati, *Nature*, 1959, **183**, 1310; J. J. Duruz and A. R. Ubbelohde, *Proc. R. Soc. London A*, 1972, **330**, 1.
5 H.-T. Nguyen, C. Destrade and J. Malthête, *Adv. Mater.*, 1997, **9**, 375.
6 B. Donnio and D. W. Bruce, *J. Chem. Soc., Dalton Trans.*, 1997, 2745.
7 D. W. Bruce, *Acc. Chem. Res.*, 2000, **33**, 831.
8 D. Fazio, C. Mongin, B. Donnio, Y. Galerne, D. Guillon and D. W. Bruce, *J. Mater. Chem.*, 2001, **11**, 2852.
9 K. Praefcke, J. D. Holbrey and N. Usol'tseva, *Mol. Cryst., Liq. Cryst.*, 1996, **288**, 189.
10 B. Donnio and D. W. Bruce, *J. Mater. Chem.*, 1998, **8**, 1993.
11 A.-M. Levelut, B. Donnio and D. W. Bruce, *Liq. Cryst.*, 1997, **22**, 753.
12 M. Kölbel, T. Beyersdorf, C. Tschierske, S. Diele and J. Kain, *Chem Eur. J.*, 2000, **6**, 3821.