Nematic mesomorphism in laterally substituted palladium complexes of alkoxystilbazoles

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Attachment of lateral carboxylate chains to polycatenar stilbazole complexes of palladium(II) unexpectedly leads to a series of materials with only nematic phases.

In the study of liquid crystals in general, a major objective is to be able to control the liquid-crystalline properties of a material *via* control of the molecular structure. As the subject advances and new types of molecules showing liquid-crystal properties appear, so there is a need to establish whether new structure–property relationships apply or whether existing principles are sufficient to understand the observed behaviour. Two of the more exciting areas of development in recent years have been the emergence of liquid crystals based on metal complexes[1] and the synthesis of polycatenar mesogens.[2]

In the former case, the field has developed rather rapidly in the last 10 years and mesogens based on metals with coordination numbers from 2 to 9 are known showing all the major phase types and exhibiting phase types and properties known for organic systems, such as ferroelectricity.[3] In addition, it is interesting to note that because of the presence of the metal centre in the molecule, the substitutional possibilities are enhanced over those offered by purely organic systems leading to materials with interesting geometric arrangements. Polycatenar liquid crystals can be defined as those with a rod-like core which possess three or more terminal chains. Much of the interest arises as these systems can show the nematic and lamellar mesomorphism characteristic of calamitic mesogens as well as the columnar mesomorphism characteristic of disk-like systems. This is best shown in systems where there are four terminal chains (tetracatenar mesogens) with each end of the molecule carrying two of these in the 3- and 4-positions of the terminal phenyl rings. In such a case, an individual mesogen can show either nematic or smectic C mesophases at short chain lengths and columnar phases at long chain lengths, with cubic phases sometimes being seen at intermediate chain lengths. A good example of this progression across a phase diagram is provided by some 5,5′-disubstituted-2,2′-bipyridines which we reported in 1998.[4]

We have for some time been interested in metal complexes of alkoxystilbazoles and have reported mesomorphic systems based on Ag(I),[5] Ir(I) and Rh(I),[6] Pd(II) and Pt(II).[7,8] In particular, we draw attention to a comparison which can be made between some complexes of Ag(I) and related systems based on Pd(II) (Fig. 1). Thus, we have reported[9] that Ag(I) complexes of 3,4-dialkoxystilbazoles bearing dodecylsulfate counter-anions (Fig. 1, **1**) show either a cubic or columnar phase depending on the chain length of the stilbazole. We have interpreted this behaviour in terms of the mesomorphism of polycatenar mesogens, but we notice that in the phase diagram, there is no sign of a smectic C phase which would be expected at shorter chain lengths. This may well be due to the presence of the dodecylsulfate anion acting as a lateral chain. Analogous complexes of 3,4-dialkoxystilbazoles have also been synthesised on palladium(II)[8] (Fig. 1, **2**) and this time we found a smectic C phase at shorter chain lengths and a columnar phase at longer chain lengths, but with no complexes showing both phases and no cubic phase at intermediate chain lengths.

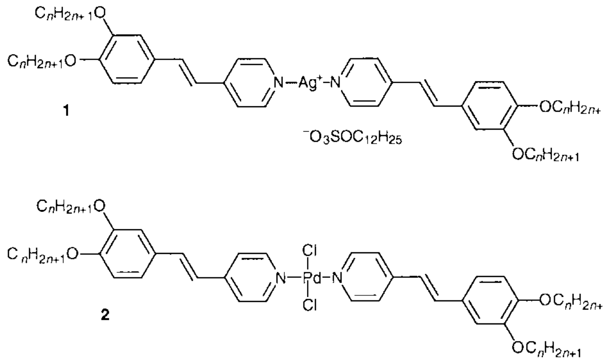

Fig. 1 Structure of dialkoxystilbazole complexes of Ag(I) and Pd(II).

We were interested, therefore, to see whether we could understand these differences in purely structural terms and so we set out to synthesise some stilbazole complexes of palladium(II) bearing lateral chains. In order to do this, we adopted an approach which we had used previously, namely to react the stilbazole with palladium carboxylates, $[Pd(O_2C–C_mH_{2m+1})_2]$, obtained from $[Pd(OAc)_2]_3$ and the carboxylic acid.[10] A number of palladium carboxylates can be obtained in this way and so reaction with 2 equiv. of dialkoxystilbazole will lead to the complexes shown in Fig. 2.

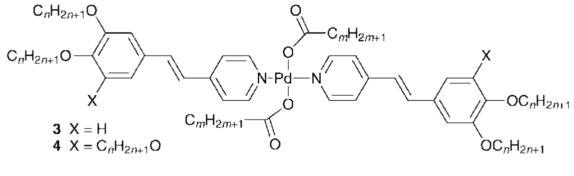

Fig. 2 Structure of the palladium complexes with lateral chains.

The reasons we adopted this approach were to do with ideas about the factors controlling the formation of lamellar, cubic and columnar phases in polycatenar mesogens. Thus, arguments are presented in which the curvature at the interface between the rigid core and the alkyl chains (Fig. 3) determine the mesophase formed in a manner analogous to that described for lyotropic systems.[11] Thus, at short chain lengths, there is no imbalance between the volumes of the core and the chains, no interfacial curvature and hence no barrier to the formation of a lamellar phase. However, at longer chain lengths, the volume required by the chains becomes much greater than that required by the core and so an interfacial curvature is established. When this curvature is large, the smectic layers are disrupted and columnar phases can form, with the columnar repeat unit being an aggregate of typically three or four molecules as shown in Fig. 4. At intermediate curvatures, cubic phases may form. Thus, it

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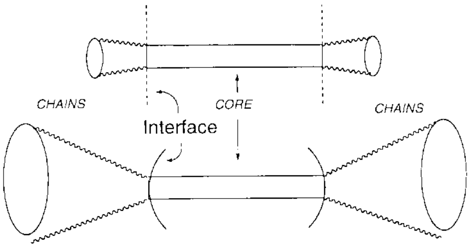

Fig. 3 Schematic to show the origin of the interfacial curvature in polycatenar mesogens.

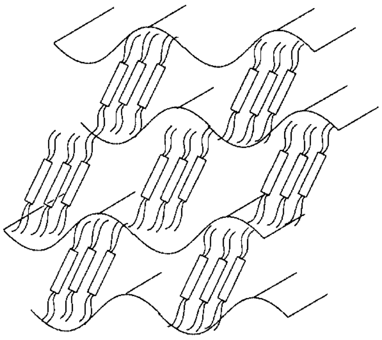

Fig. 4 Schematic to show the break-up of a lamellar structure into columnar units.

is possible to view phase formation as being dependent on the balance between the volume of the mesogen core and its chains.

We therefore speculated that in the case of the palladium mesogens, the rate of change of the volume of the chains (four methylene groups per homologue – *i.e.* about 108 Å^3) was quite rapid for the size of the core and so the transition from lamellar to columnar behaviour would be rather rapid as a function of the chain length accounting for the fact that this transition happens at a given chain length. Therefore, we reasoned that we could influence the volume of the core by introducing lateral substituents, and so modulate the effect of the increase in the chain volume. To this end, we synthesised a number of complexes **3** (Fig. 2) in which we varied the stilbazole chain length and the carboylate chain length.

The results are summarised in Table 1 and show somewhat unexpected phase behaviour. Thus, for all dialkoxystilbazoles examined with all carboxylates from butanoate upwards (shorter carboxylates did not give mesomorphic materials), only a nematic phase was seen. Previously, Maitlis and coworkers[7a] had shown that palladium complexes of *mono*alkoxystilbazoles with lateral carboxylates gave nematic phases, consistent with the known behaviour of organic systems where the introduction of lateral chains suppresses smectic phase formation.[12] Other examples of lateral substitution in metallomesogens may be found as compounds **24–39** in ref. 1*a*. However, here we are dealing with a polycatenar mesogen and so we might expect the lateral chains to behave differently, particularly when the chain length on the stilbazole was long. Thus, we might have expected to see a smectic C or columnar phase depending on whether the chains added to the core or radiated out, respectively. Curious then to pursue this further, we extended the approach by accessing the complexes **4** in whch we used a 3,4,5-trialkoxystilbazole ligand. All of the palladium dichloride complexes of these ligands which were mesomorphic showed a columnar mesophase[8] and so we reasoned here that by increasing the volume of the core with the lateral chains, it would be possible to find smectic C or even cubic phases. Alternatively and perhaps most likely, the complex would simply behave as a classical discotic mesogen with eight peripheral chains and continue to show a columnar phase. Table 1 shows that even these thoughts were misplaced and once more we found complexes which showed only the nematic phase. Thus, for compounds of this type with six or eight peripheral chains to show only nematic phases is, we believe, unprecedented.

Table 1 Thermal data for the new complexes

n	*m*	Transition	*T*/°C
Compound **3**			
6	3	Crys–I	181 (decomp)
12	3	Crys–N	111
		N–I	123
6	5	Crys–N	125
		N–I	131
12	5	Crys–N	95
		N–I	109
6	7	Crys–N	115
		N–I	123
12	7	Crys–N	90
		N–I	100
Compound **4**			
14	3	Crys–N	69
		N–I	77
14	7	Crys–I	55
		(N–I)	(53)

The questions now arise as to the nature of the nematic phases of these complexes and why they arise. Are the nematic phases of complexes **4** 'discotic nematic' or are they composed of more rod-like systems, *i.e.* how are the chains arranged? What is the behaviour of the lateral chains in these systems which causes the formation of only nematic phases irrespective of the nature of the ligands and unrelated to the phases formed by the parent dichloride systems? These are clearly quite unique materials which require further detailed study both to ascertain why nematic phases are formed exclusively and how their mesomorphism contributes to the understanding of the mesomorphism of polycatenar liquid crysals. It is also important to note that a study of this type is greatly facilitated by the substitutional possibilities offered by the metal centre.

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