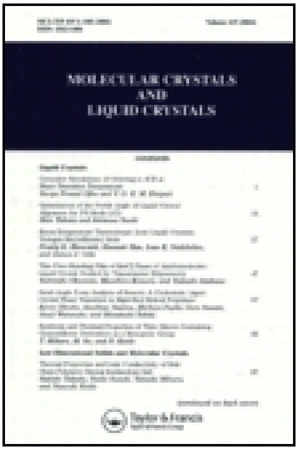

Molecular Crystals and Liquid Crystals

Polycatenar Metallomesogens - From Layers to Columns and so yo Cubics

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POLYCATENAR METALLOMESOGENS – FROM LAYERS TO COLUMNS AND SO TO CUBICS[§]

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The mesomorphism of various series of polycatenar metallomesogens is described and, by considering various structure/mesomorphism arguments, a model is proposed to rationalise cubic phase formation in calamitic and polycatenar mesogens.

Keywords: polycatenar; liquid crystals; metallomesogens; phenanthrolines; palladium; platinum; silver

INTRODUCTION

Columnar mesophases are distinct from lamellar systems in that in the mesophase, it can be considered that the molecules arrange themselves into columns which then subsequently organise into some two-dimensional

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[§] Dedicated to the authors of reference 3 in recognition of their seminal work in opening another chapter in the story of liquid crystals.

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arrangement. Thus, the order of the system is characterised by the one-dimensional ordering of the constituent molecules within the column and the two-dimensional arrangement of the columns. The term ***columnar*** implies the situation just described where columns are formed by the arrangement of molecules and where mutual, intracolumnar interactions may be influenced by dispersion forces or occasionally by weak, non-covalent interactions such as hydrogen bonds or intermolecular dative covalency, as well as by steric and space-filling constraints. Columnar mesophases are known in the study of both thermotropic and lyotropic mesogens and in the latter case, they have also been referred to as 'chromonic' [1], although the term columnar is preferred as it allows a better appreciation of the relationship between similar phases formed in different ways by different systems.

While columnar mesophases have been known for many years through the work of, for example, Luzzatti and Skoulios [2] with simple metal carboxylates, they came to particular prominence in the late 1970 s when Chandrasekhar, Sadashiva and Suresh reported [3] the synthesis of hexaesters of hexahydroxybenzene (**1**) which are accepted as the first ***discotic*** mesogens showing columnar phases. In the subsequent years, this led to some confusion in nomenclature and the phases were often referred to as 'D' – discotic – a term which reflects the shape of the molecule rather than anything about the organisation within the phase [4]. This term is now replaced by 'Col' – which does describe the nature of the phase – and this is particularly helpful for the molecules which will be described in this manuscript which, like the metal carboxylates, do form columnar phases but are not discotic. Of course, this reference is to ***polycatenar*** mesogens – mesogens constructed with a molecular core which is typically like that found in a calamitic mesogen, yet having three or more terminal chains [5]. In this manuscript, we shall explore the behaviour of several tetracatenar mesogens and see how aspects of the molecular structure affect the mesomorphism.

THE MESOMORPHISM OF TETRACATENAR MESOGENS

As is now quite well known, tetracatenar mesogens in which the terminal chains are attached symmetrically in the 3,4-positions (**2**) have a most interesting mesomorphism. Thus, they show nematic and/or SmC phases at short chain lengths, while when the chain length is longer, columnar phases result. Of interest in this behaviour is to understand:

- the origin of the SmC phase;
- the nature of the columnar phases;
- the nature of the cross-over between the lamellar SmC phase and the columnar phases;

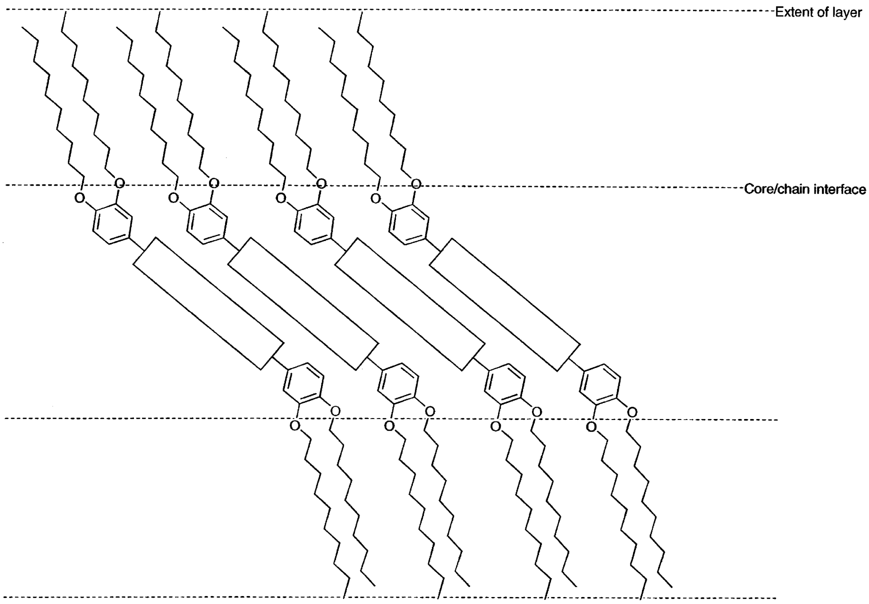


FIGURE 1 SmC phase of tetracatenar mesogens.

- how the above may be related to the structure and nature of the mesogen.

In considering the smectic phase, it is noted that the SmC phase is always and uniquely observed due to the fact that at the interface between the rigid core and the chains, the cross-sectional area of the chains in greater than that of the core and so to fill space effectively, the cores must tilt (Fig. 1). The extent of this tilt has been determined experimentally and found to be in the region of 50° for the cores and 20° for the chains [6].

However, as the chains grow in length and/or as the temperature increases, the chains begin to occupy a greater volume and, in order to accommodate this additional volume requirement, the cores tilt even further. However, this can only continue so far and eventually, the situation is reached where the smectic layers can no longer hold together and they break up, leading to a phase transition.

The phase that forms above the SmC phase is of some interest and classically, it is often considered that the transition is to a columnar phase through the intermediacy of a cubic phase as exemplified, for example, by the behaviour of tetracatenar bipyridines [7]. Alternatively, of course, the transition may happen directly as illustrated in Figure 2 [6], and here one would expect to find the stability of the columnar phase increasing as that of

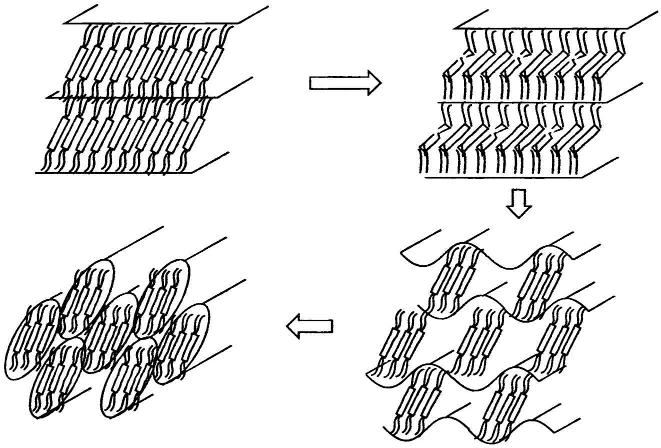


FIGURE 2 Schematic of the direct transition from SmC to columnar phase (arrows represent either increasing temperature or chain length).

the SmC phases decreases, so that certain homologues show both phases. Thus, it might be assumed that the transition out of the SmC phase depends on the length of the terminal chains, the temperature, the volume of the molecular core and its cross-sectional area at the core-chain interface. It is, then, also necessary to suggest that the stability of the phase formed subsequently (cubic or columnar) is a function of the same parameters.

TETRACATENAR COMPLEXES OF SILVER(I)

The structure of the complexes (**3**) is described by the linear coordination of two 3,4-dialkoxystilbazoles about the silver centre with an attendant anion which is associated closely with the silver cation [8].

In pursuit of the assertions given above which concern the transition out of the SmC phase, it is instructive to consider two phase diagrams (Figs. 3a and 3b). The former shows the mesomorphism for a series of complexes **3** where X^- is the relatively small triflate (OTf) anion ($CF_3SO_3^-$), while the latter considers the behaviour where X^- is the larger dodecylsulphate (DOS) anion ($C_{12}H_{25}OSO_3^-$).

In considering these phase diagrams, it is important to note first that neither series shows a SmC phase, something which we would expect of tetracatenar materials of this type. This we attribute [9] to the presence of the lateral anion and the way it affects the ability of the molecules to pack in the mesophase. Then, on examination of the phase diagrams we see that they adopt a similar form in that a cubic phase is formed which decreases in

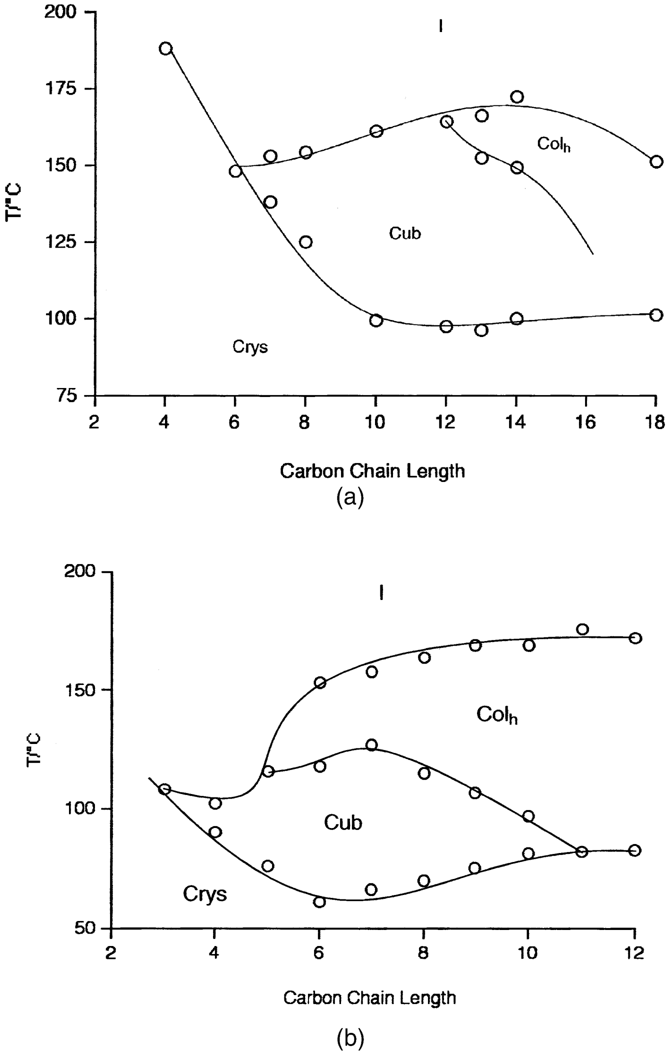


FIGURE 3 Phase diagrams for bis(3,4-dialkoxystilbazole)silver(I) with triflate (a) and dodecylsulphate (B) anions.

stability as the chain length increases, giving was to a Col$_h$ phase. The first point of significance is that for the triflate salts, the cubic phase extends until the terminal chains contain fourteen carbon atoms, while for the DOS salts it extends only to the decyloxy homologues. Similarly, the Col$_h$ phase appears with a terminal chain length of $C_{11}H_{23}$– for the triflates, whereas it is present at a chain length of C_6H_{13}– for the DOS materials.

From single-crystal X-ray studies [10], we know that while octylsulphate anions lie alongside the molecular core comprising the stilbazoles unit, but do not extend past it, DOS anions *do* extend past this core and so must be considered as contributing in part to volume (and cross-sectional area) associated with the terminal chains. Therefore, adopting the arguments advanced above, we would conclude that in comparing the triflate and DOS salts, the fact that the DOS anion contributes to the volume occupied by the terminal chains is most significant and means that the curvature and volume requirements imposed for the formation of the columnar phase over the cubic are met at shorter lengths of the ligand terminal chains.

That this is a reasonable conclusion is further demonstrated for a series of complexes **3** where $X^- = C_mH_{2m+1}OSO_3^-$ (Fig. 4) [11]. Thus, it is readily apparent that a combination of ligand and anion chain length determines the mesomorphism, so that with short ligand chains (Fig. 4a), anion chains which extend past the stilbazole core are required to induce a mesophase

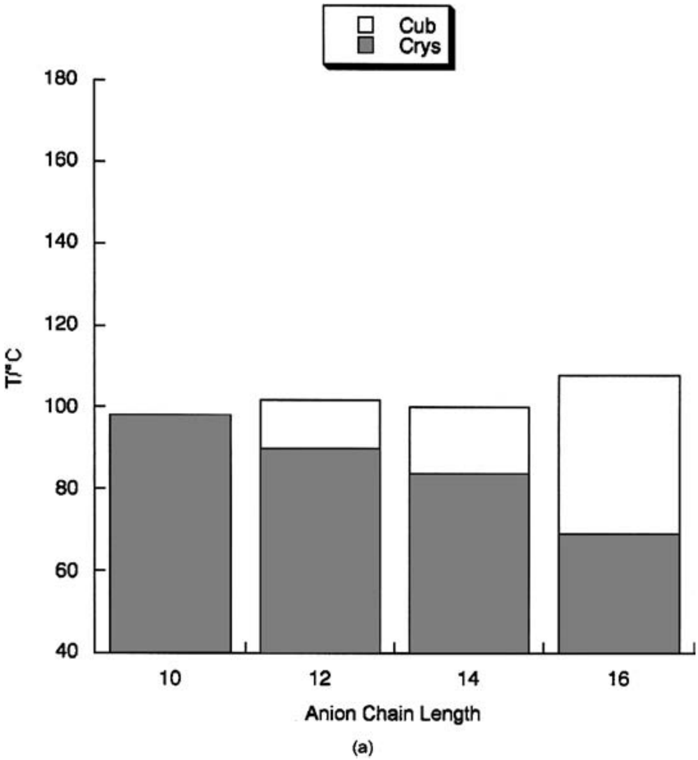


FIGURE 4 Histogram representation of the mesomorphism for a series of silver complexes **3** with (a) $n = 4$, (b) $n = 6$, (c) $n = 12$ with anion $C_mH_{2m+1}OSO_3^-$

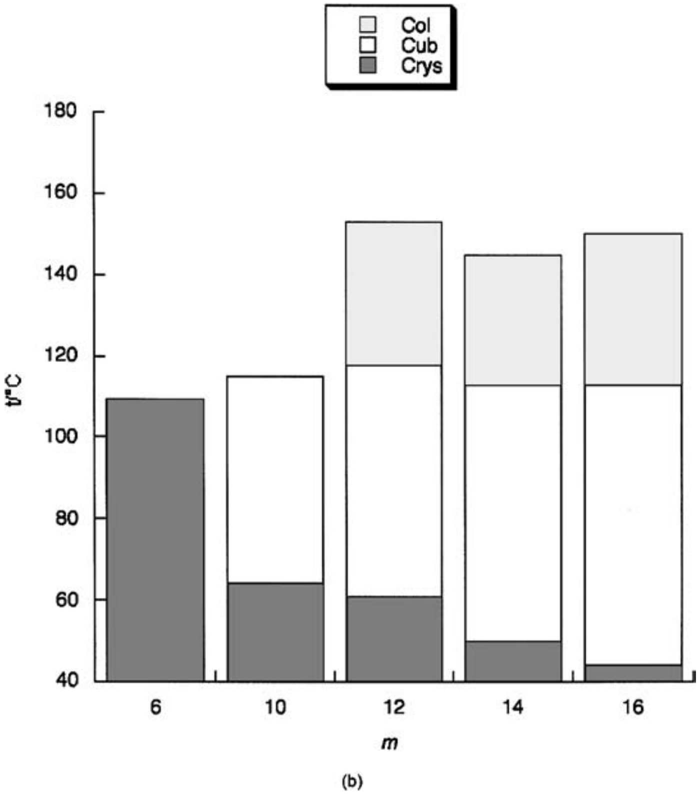


FIGURE 4 Continued.

(cubic), while when the chain is longer (C_6H_{13}–; Fig. 4b), a cubic phase is observed in each derivative, with columnar phases appearing when the anion chain extends past the core. When the ligand chain is further extended ($C_{12}H_{25}$–; Fig. 4c), cubic phases are seen for only two derivatives, but as soon as the anion extends past the core, the mesomorphism is entirely that of the columnar phase.

These conclusions are further supported by the results of lyotropic studies carried out on these mesogens [12]. Thus, a derivative of **3** ($n = 4$; $X^- = C_{14}H_{29}OSO_3{}^-$) shows a cubic phase as a thermotropic material (Cr • 84 • Cub • 102 • I) and yet on addition of small, apolar solvents (MeCN, DMF, DMSO), an additional lamellar L_α phase was observed. Similarly, a related derivative (**3**; $n = 6$, $X^- = C_{14}H_{29}OSO_3{}^-$) which is also cubic as a thermotropic material (Cr • 50 • Cub • 113 • Col_h • 145 • I) similarly shows an induced L_α phase using the same solvents. These solvents are expected, by their nature, to associate predominantly with the polar core of the molecule

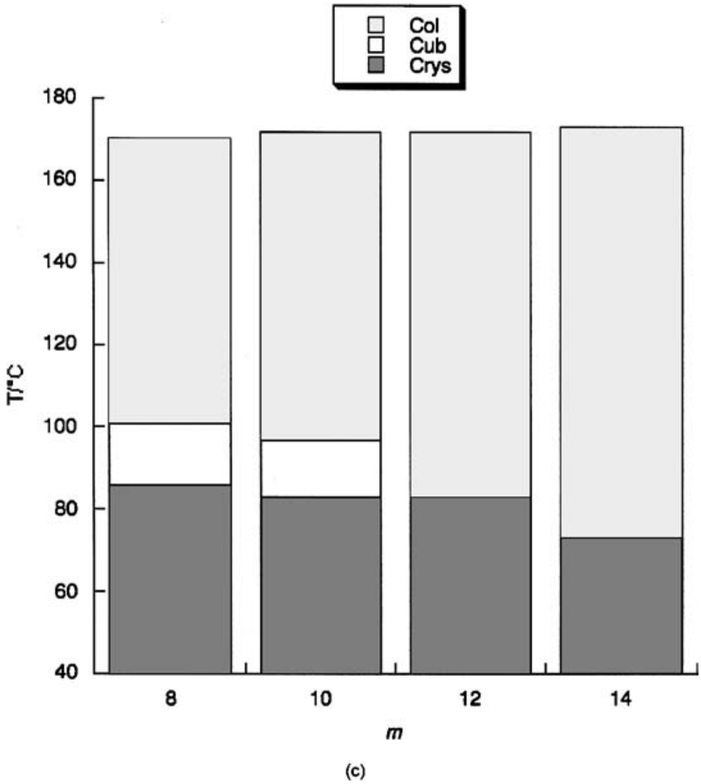


FIGURE 4 Continued.

where the silver cation and charged part of the anion are found, and hence they increase the effective volume of the core part of the complex promoting the formation of a lamellar phase (*i.e.* a phase with no surface curvature).

However, using longer-chain alcohols which are more lipophilic, the mesomorphism is changed in a different way and columnar phases are induced, consistent with these solvents enhancing the amount of peripheral chain (‘external solvent’ [13]) in a similar way to that found in ternary lyotropic systems. One final observation is that when short-chain alcohols are added, a nematic phase is induced which is interpreted as resulting from the disruption of intermolecular interactions by these small solvent molecules.

TETRACATENAR COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

Having investigated the mesomorphism of the silver complexes, we then turned our attention to analogous materials based on palladium(II) and platinum(II) shown as compound **4** [14]. We found that for the most part, the behaviour of the complexes of both metals was very similar and so we will concentrate our discussion on the palladium complexes which have been studied more extensively.

The phase diagram as we now describe it is shown in Figure 5. At shorter chain lengths, a SmC phase is found, typical for tetracatenar mesogens. At the longest chain lengths, the mesomorphism has changed to show a columnar hexagonal phase which is again in keeping with the classical behaviour of tetracatenar species. However, on the basis of optical microscopy, we had believed originally that the $\mathrm{Col_h}$ phase appeared first in the homologue with $n = 13$, but X-ray diffraction showed that for $n \leq 13 \leq 16$, the phase was, in fact, lamellar and yet the optical texture [15] is very like that of a columnar phase. The nature of this lamellar phase has been discussed elsewhere, but its significance is that it shows a new way of moving from a SmC to a columnar phase in tetracatenar mesogens. Thus, unlike many classical cases, there is no cubic phase and what is also most surprising is that the change from one phase to the next is most abrupt, so that in adding a single methylene group to each chain, it is possible to move from SmC to lamellar phase ($n = 12$ to $n = 13$) or from lamellar phase to columnar phase ($n = 16$ to $n = 17$).

Indeed, we find that sudden transitions from lamellar to columnar mesomorphism turn up elsewhere and recently [16], we have found that in

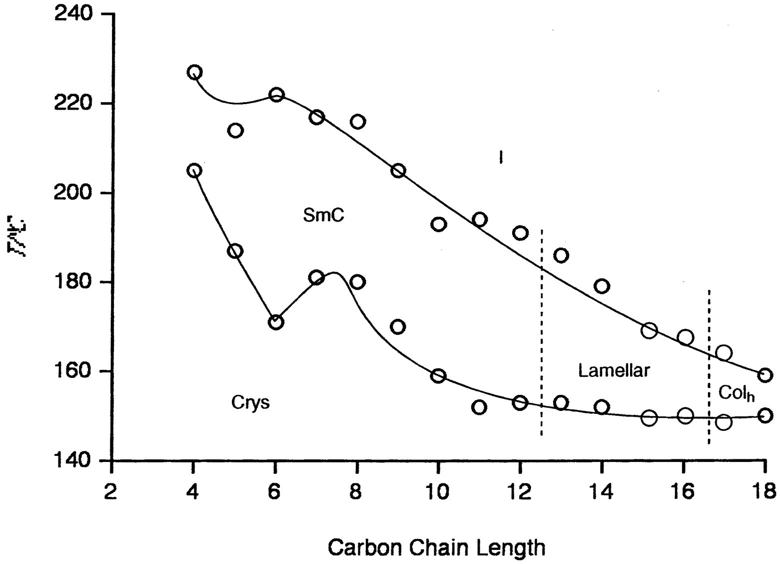
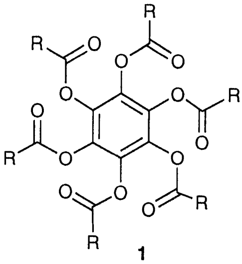
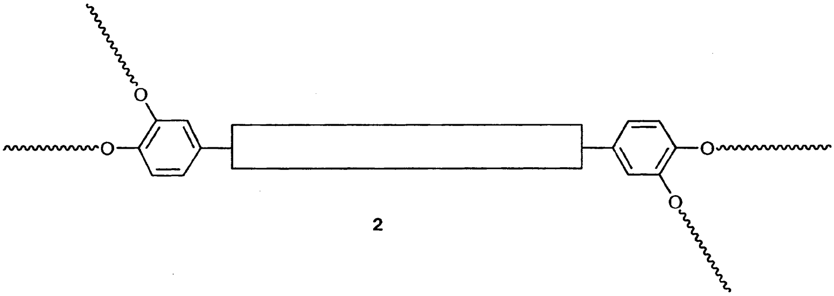


FIGURE 5



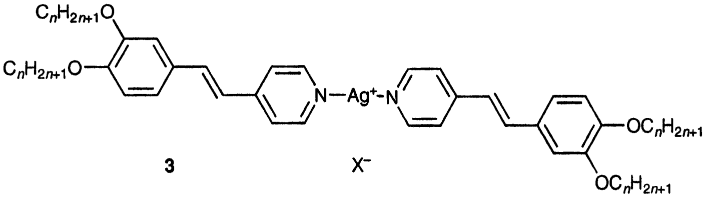
1

COMPOUND 1



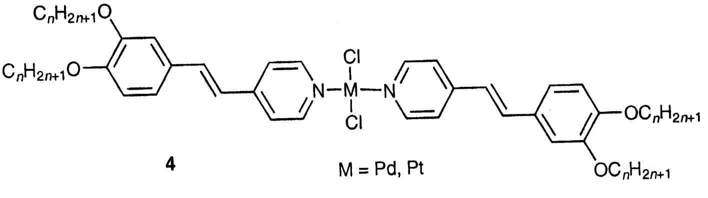
2

COMPOUND 2



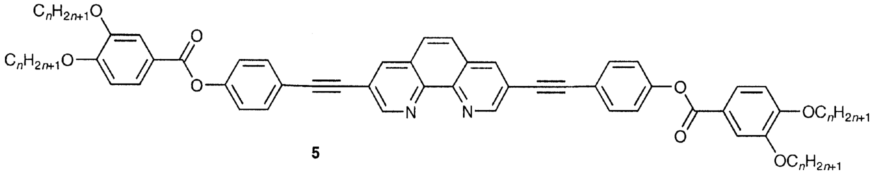
3 X^-

COMPOUND 3



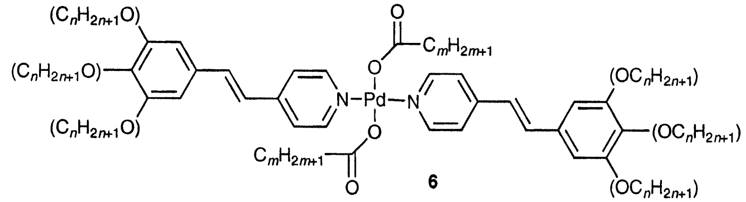
4 M = Pd, Pt

COMPOUND 4



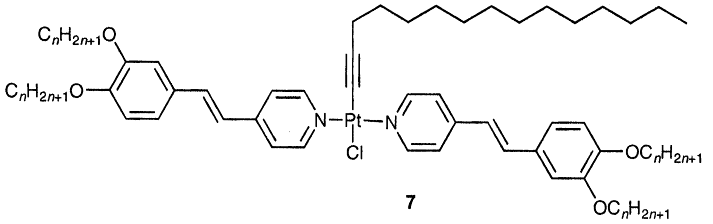
5

COMPOUND 5



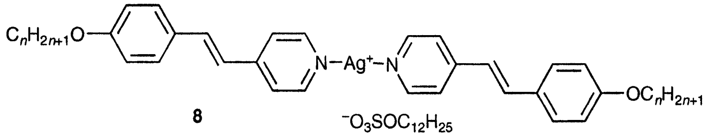
6

COMPOUND 6



7

COMPOUND 7



8

COMPOUND 8

a series of 3,8-disubstituted, tetracatenar, 1,10-phenanthrolines, the mesomorphism changed abruptly from SmC at one chain length to $\mathrm{Col_h}$ in the next, with no compounds showing both phases. Thus, it is clear that there is some way to go before we can identify clearly the factors which dictate mesomorphism at this cross-over between phases.

So returning to the palladium and silver systems, we can see two distinct patterns of mesomorphism, where in one case (silver) there is a rather smooth transition into the columnar phase as the chain length increases, whereas in another (palladium), the transition is abrupt. Comparison of the molecular structure of these two families reveals that in the case of silver, however, there is a lateral (anion) chain. As we have demonstrated the effect that such a chain can have on the stability of lamellar, cubic and columnar phases, it seemed appropriate to attempt the synthesis of palladium analogues with such chains. This was achieved (**6**) and the results were rather unexpected, in that looking at the structure (the parentheses in the structure of **6** indicate that a large variety of substitution patterns were investigated) one might expect that columnar phases would result, but in fact, all examples studied, irrespective of degree of substitution or chain length, showed a nematic phase if they were mesomorphic [17].

Of course, this is still not a true comparison, for while these palladium complexes have two lateral chains, the silver complexes on which they are modeled have only one, and so it was necessary to adopt a new strategy to effect a comparison between the two series of materials. This was achieved using platinum chemistry, for if we are to add a single chain and thereby synthesise a complex of lower symmetry, we require the additional inertness offered by platinum over palladium.

In the course of this work, we investigated a variety of potential long-chain ligands including carboxylates and thiolates, but in our hands, all were resistant to the aim of effecting monosubstitution at the metal centre. Eventually, however, by using rather short reaction times, we were able to make mono-acetylide complexes (**7**) and by using a 1-pentadecyne ligand (fifteen atoms), we were able to mimic the chain length of the DOS anion (fifteen atoms in total - twelve carbons, plus two oxygens and a sulphur from the sulphate group) [18]. On examination of the mesomorphism of these complexes, we were somewhat surprised to find that all were nematic and that some showed, in addition, a SmC phase.

DISCUSSION

So what might we conclude from the observations above? We believe that in synthesising **7**, we have a good structural model of complexes **3** and so the difference in mesomorphism, in particular as it relates to cubic phase formation, must go further than a simple structural analogy. The clue comes in considering the phase behaviour of some silver(I) stilbazole complexes reported [19] before the polycatenar derivatives and shown as **8**. These complexes were shown to form N, SmC, SmA, cubic and the tetragonal S_4 [20] phases. Once it is realised that the anion is closely associated with the cation in these species and that they behave, in effect, as neutral materials, then the observation of the nematic phase comes as little surprise as in calamitic systems with lateral chains, the nematic phase is the only one observed [21]. However, in this light, what is more difficult to understand is why the smectic phases form. In considering this problem, Levelut [22] proposed that the extra factor stabilising the lamellar phases was an intermolecular, ionic interaction between oxygens on the sulphate group and neighbouring silver cations. Thus, while clearly not too strong an interactions (witness the formation of the nematic phase at short chain lengths), in combination with the lengthening terminal chains it is sufficient to stabilise lamellar phases.

The acceptance of such an intermolecular interaction then suggests that the presence of specific intermolecular interactions ought to be considered in interpreting cubic phase formation, and this idea was advanced in a review by Diele and Göring [23] and was further developed in subsequent articles [15,24,25]. The model then appears to fit a very wide range of materials and, while it is not predictive, it is certainly able to rationalise cubic phase formation in a wide variety of materials.

So where do discotics fit into all this? Well, in some ways they don't and yet in others they are central. The above work excludes any molecules which may be described as 'discotic' yet it has relied extensively on columnar phases, interest in which grew enormously as the result of reference 3. Thus, as columnar phases subsequently became well-recognised, so it was that the mesomorphism of polycatenar systems could be more readily appreciated.

The story told above started in calamitic systems, moved to materials with columnar phases and through both strands of the work ended up with what we believe is a greater appreciation of cubic phases. Had we set out to do this work in a very deliberate way, I am sure we would not have got near to the compounds and arguments contained herein, but that is the nature of the subject and seminal papers such as reference 3 have effects far beyond those ever imagined at the time of writing.

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