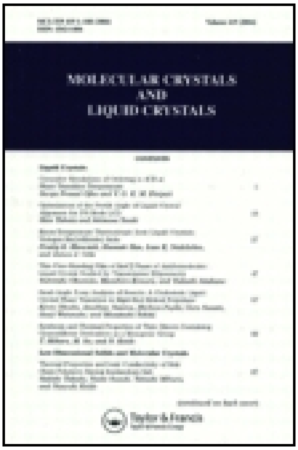

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On the Formation of Cubic Phases

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On the Formation of Cubic Phases

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Ever since the report of the S_{III} phase by Gray in biphenylcarboxylic acids,[1] there has been interest in what was termed the 'smectic D' phase, and what we now know of as the cubic phase (Cub). A recent review of the subject by Diele has collected together very many of the compounds known to show such phases and has looked at structural types. [2]

In the course of our work with metallomesogens [3] and with polycatenar liquid crystals, we have found several materials with cubic phases and we have become interested in the formation of the phases and the transitions into and out of them. Because we have encountered them in several different types of compound, we have been able to make certain comparisons between them, and we have noted common features and other aspects which appear disparate. It is still our view that there are aspects of the cubic phase which remain a mystery, but in this short article, we hope to try to bring together some of our thinking to stimulate further thought and work on the subject.

The first cubic materials which we encountered were complexes of silver(I) with the structure shown in Figure 1. The first silver complexes of this type which we had synthesised possessed tetrafluoroborate anions (X = BF_4) and showed very high transition temperatures. [4] We therefore introduced the dodecylsulphate anion (X = $C_{12}H_{25}OSO_3$) in a simple attempt to reduce the transition temperatures. [5] This it demonstrably did, and we encountered materials with nematic, smectic and cubic phases (Figure 2).

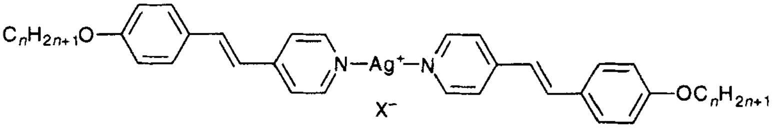

Figure 1 Mesomorphic complexes of silver(I)

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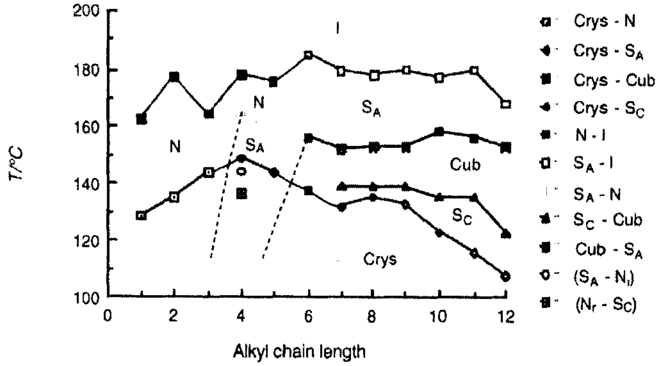

Figure 2 Phase diagram for the silver(I) dodecylsulphate salts

Several points arise from a consideration of these complexes. First, is that they are formally ionic and yet show a nematic phase; as such they are virtually unique. However, measurements showed no conductivity in the nematic phase and, therefore, we assume that the cation and anion are related as tight-bound ion pairs. However, they *do* form two smectic phases, namely smectic C and smectic A. This is remarkable as calamitic molecules possessed of lateral chains invariably show nematic phases only, as the lateral chain disrupts totally the formation of smectic phases. Last, and by no means least, seven of the materials show a cubic phase which is in all cases below a smectic A phase and is, in all but one case, above a smectic C phase.

Synthesis of laterally fluorinated derivatives of these materials showed how fragile the cubic phase was in that it was absent in one isomer (3-fluorination) and present in the other (2-fluorination).[6] Another outcome of this work was a complex which had a cubic phase below a nematic phase. In collaboration with Levelut, this enabled us to obtain aligned nematic phases from which monodomain cubic phases were realised, allowing the symmetry of the phase to be identified as $Ia\bar{3}d$.[7]

We then went on to look at the effect of the alkylsulphate chain length on the stability of the cubic phase, and found that for octyl- and decyl-sulphate anions, the cubic phase was absent, while for the tetradecylsulphate anion, the cubic phase returned. [8] A single crystal structure of an octylsulphate complex provided some clue as to the reasons behind these observations, as we found that in this material, the lateral alkylsulphate chain did not extend beyond the rigid, aromatic core of the complex. The same situation would also be true for decylsulphate complexes, while measurement showed that for chain lengths longer then dodecyl, the lateral chain *would* extend beyond the molecular core.

With Levelut, we then used these observation to discuss aspects of the formation of the cubic phases. We advanced ideas related to the interfacial curvature between the aromatic and aliphatic part of the molecules and the contribution that a lateral alkylsulphate chain would make depending on whether or not it extended beyond the rigid core. [7]

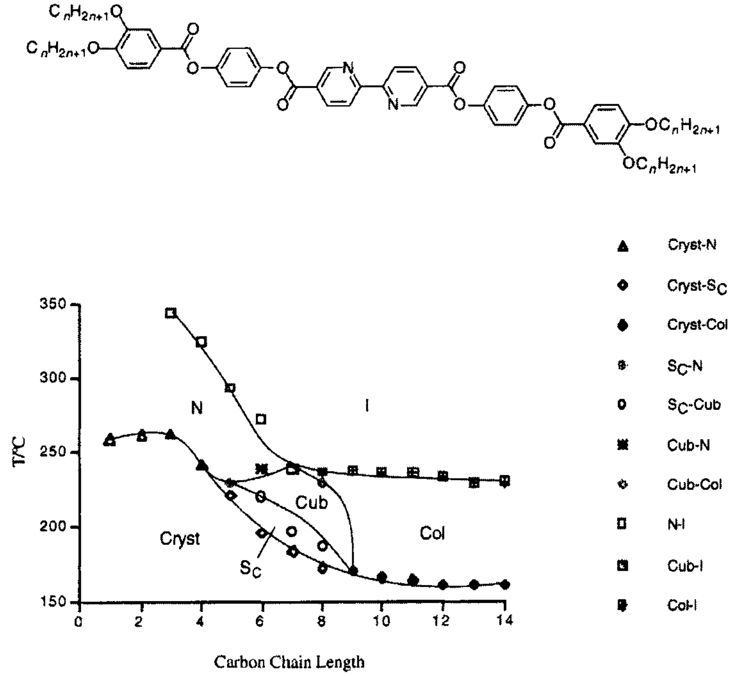

Figure 3 Phase diagram for the illustrated tetracatenar 2,2'-bipyridines

Polycatenar Systems

We and others have also looked at polycatenar mesogens, [9] where cubic phases have been found. In symmetric polycatenar materials, they are invariably found in either doubly swallow-tailed compounds, or in tetracatenar compounds with terminal 3,4-disubstitution. In both cases, the cubic phase is mostly seen above the smectic C phase, although occasionally it is found to appear below or above the columnar hexagonal phase. A rather classic example of the mesomorphism of tetracatenar compounds was in our recent report [10] of mesomorphic 2,2'-bipyridines, where the progression with increasing chain length from nematic and smectic C phase through the cubic and onto columnar phases was rather well demonstrated (Figure 3). However, it is not the case that phase diagrams of this sort are always found and in other, metal-based systems, we have found examples where, with increasing chain length, the system simply switches over directly from smectic C to columnar behaviour (Figure 4), [11] with no materials exhibiting both phases, and no sign of a cubic phase. Thus, on increasing the terminal chain length, it is possible to move from the nematic and lamellar (S_C) phases to a columnar phase, either directly or through the intermediary of a cubic phase.

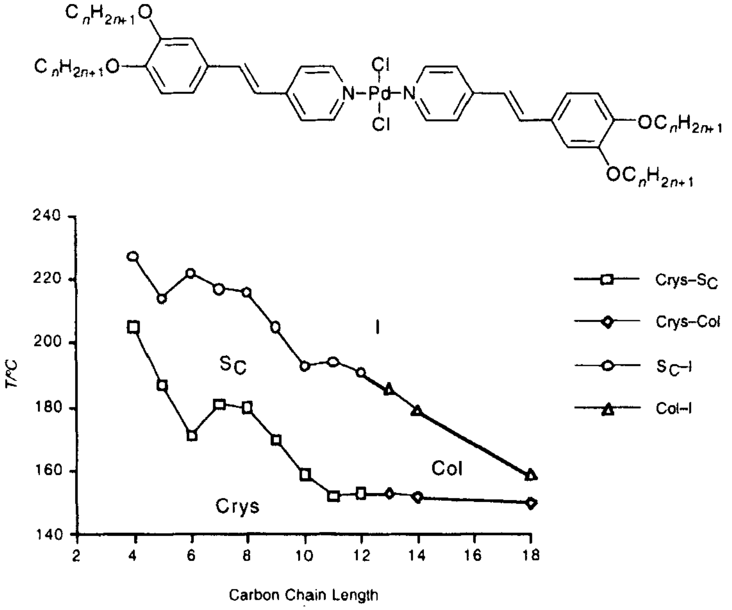

Figure 4 Phase diagram for the illustrated tetracatenar palladium complexes

It is perhaps interesting to compare these two systems and to speculate why the form of the phase diagrams is different. In the case of the bipyridines, the aromatic core is rather extended, occupying a larger volume than that of the aromatic core of the metal complexes. In the latter case, addition of methylenes in groups of four (in moving from one homologue to the next), leads to a relatively large incremental change in the volume of the aliphatic chains compared to that of the core; the change in relative volumes being seen as an indirect measure of the interfacial curvature. However, in the case of the bipyridines the core volume is much larger and so the incremental change in volume ratios is relatively smaller. This more gradual change in the case of the bipyridines leads to a progression from smectic C to columnar through the cubic phase, while the larger changes in the metal complexes lead to a more pronounced and dramatic progression.

Kékicheff [12] has previously proposed models based on undulating layers to explain transitions from lyotropic lamellar to hexagonal phases through various intermediate phases, and Guillon [13] has recently advanced a similar explanation for the lamellar-to-columnar transition in thermotropic materials. Further, in collaboration with Guillon, we [14] advanced a similar mechanism to account for the columnar-to-cubic transition. These undulations arise from the mismatch between the surface area required by the rigid core of the molecule at the aromatic/paraffinic interface, and the surface area required by the chains at the same interface, i.e. it is a manifestation of the aromatic/aliphatic interfacial curvature.

Discussion

So where is this taking us? Let us start by realising that the mesomorphism of the polycatenar materials discussed above can be explained in terms of the curvature which develops at the aromatic/aliphatic interface, and that no further level of explanation appears necessary. Of course, we do not understand why in some cases the phase behaviour evolves directly from lamellar to columnar phases, while in others it relies on the intermediary of a cubic phase, but that simply emphasises our lack of proper understanding of the factors which affect the formation of the cubic phase.

However, if we look to Diele's review of materials [2] forming cubic phases and discount the polycatenar materials and a small number of disc-like systems, then we are left with, in effect, materials which may perhaps be classified into five groups:

i) Gray's biphenylcarboxylic acids;

ii) Demus' hydrazines;

iii) carbohydrates/diols (most of which possess two terminal chains at one end of the molecule and might possibly be classified as polycatenar if it is assumed that they dimerise);

iv) amides, all of which possess terminal 3,4-disubstituted phenyl rings;

v) our silver salts.

What all of these materials have in common is the ability for significant intermolecular interactions through the centre of the molecules (i.e. all hydroxyl or carboxylate systems are assumed at least to dimerise). In the case of our silver complexes, this point was well brought home in an argument advanced by Levelut. [7] Recall that these complexes show not only nematic phases, but two lamellar phases (S_A and S_C) and recall also that lateral chains invariably lead simply to nematic phases. That we see any lamellar phase at all in these materials *must* be due to the presence of some other intermolecular interactions, in this case ionic interactions between tight-bound ion pairs. We therefore advanced that the ionic interactions were important in stabilising the cubic phase.

What in fact we are saying is that we can identify two mechanisms for cubic phase formation. One, which is rather clear, relies simply on the ideas of interfacial curvature advanced above. However, the other seems to rely on the possibility for rather specific intermolecular interactions (i.e. not simply dispersion forces).

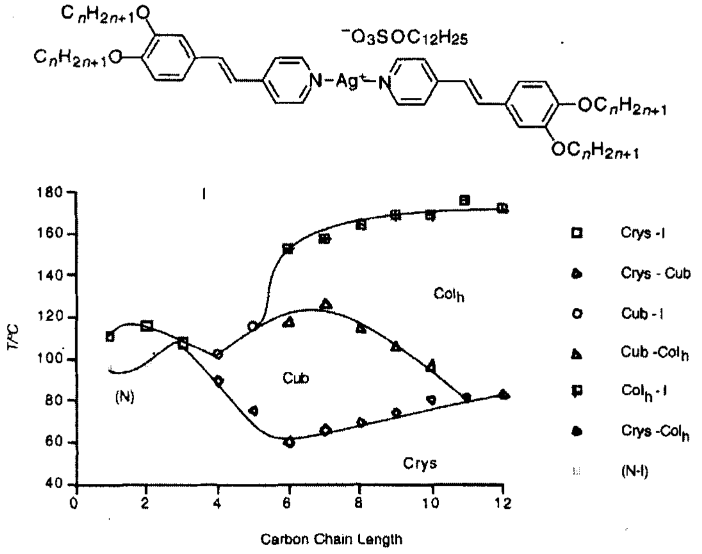

Figure 5 Mesomorphism of the illustrated tetracatenar silver(I) complexes

Now, what happens if we combine the two possibilities and look at truly polycatenar systems (i.e. not the carbohydrates or amides) which have the possibility for intermolecular interaction. We can do this by considering the mesomorphism of some polycatenar mesogens of silver(I), shown in Figure 5. [14] Here, we can see that no smectic C phase is found (the nematic phase at short chain length is due to dissociated, monoligand species and so strictly cannot be compared), and that only cubic and columnar phases are found.

Here, we can argue that the combination of the lateral chain and the two extra chains in the terminal 3-positions, destabilises both the nematic and lamellar phases. Thus, the presence of both the ionic interactions and the surface curvature effects do not destructively interfere, and the mesomorphism is that of a polycatenar material which shows the cubic phase. These findings are further supported by other results we have obtained with silver complexes of 3,4-dialkoxystilbazoles possessing alkylsulphate anions of varying chain length. [15]

However, we can perhaps develop the idea of the importance of the ionic interaction by reference to some complexes of palladium(II). Thus, in collaboration with Maitlis we had previously shown that lateral chains could be added to palladium(II) complexes of simple stilbazoles to reduce transition temperatures and generate nematic phases. [16] If we now prepare polycatenar palladium(II) complexes containing lateral chains (Figure 6), we find that the mesomorphism is entirely that of the nematic phase. Now there are no lateral interactions and so neither the mesomorphism of polycatenar materials, nor a cubic phase, is seen. [17]

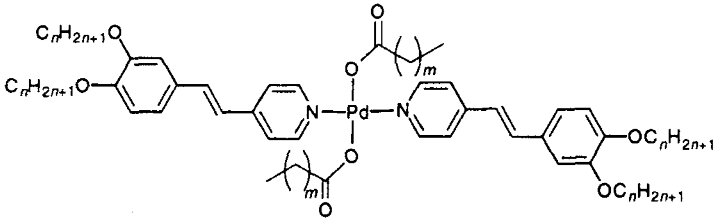

Figure 6 Laterally substituted, tetracatenar complexes of palladium(II)

Conclusion

What we have tried to do in this article is to identify two separate features required for cubic phase formation, namely simple interfacial curvature, and the presence of intermolecular interactions. The article takes some of our initial ideas from reference [7], and some similar ideas from the later review by Diele [2] and expands upon them in some detail using examples which were not available when the review was written. Certainly the ideas account for essentially all systems which might be regarded as being based on a rod-like core. We have also looked at systems which possess the essence of both features and found a consistency there, which leads also to a demonstration of the significance of ionic interactions in the mesomorphism of certain polycatenar metal complexes. Of course, none of this considers the micellar cubics described by Tschierske [18] and by Percec and Ungar [19] - their formation is different again!

Acknowledgements

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