On the Formation of the Thermotropic Cubic Phase: Insights from Monoacetylide Complexes of Pt(II)

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In the liquid crystal phase behavior of surfactants, cubic phases are common and can, in principle, be found between any pair of adjacent phases.[1] In a binary water/surfactant phase diagram, the formation of phases as a function of water content depends on interactions between the polar headgroups and the water solvent, and also on the size of the polar headgroup versus the volume occupied by the hydrophobic chains. In an organized assembly of these surfactant molecules, one can imagine that a surface between the two incompatible parts, that is the hydrophilic and hydrophobic parts, is generated and that this interface possesses a variable curvature, with the degree of curvature depending on the above parameters. Thus, the formation of a particular phase depends strongly on the idea of interfacial curvature, that is the curvature at the hydrophilic/hydrophobic interface.

In thermotropic liquid crystals, there exists a family of mesogens where interfacial curvature is also crucial in determining the phase behavior.[2] These are the polycatenar mesogens[3] which are composed of an extended, rigid core and three or more terminal chains and here the interface in question is that between the aromatic core and the terminal alkyl chains. Of these mesogens, perhaps the most interesting are those with four terminal chains with two found at each end in the 3,4-positions of phenyls rings. Here, at short chain lengths, nematic and smectic C phases are formed, while at longer chains lengths, columnar phases are observed. The lamellar (S_C) phase forms because in order to accommodate the greater cross-section of the chains relative to the core, the core tilts. However, as the chains grow longer, they occupy a much greater volume compared to the core which induces curvature in the lamellar phase, causing the lamellae to break down and forming a columnar phase composed of aggregates of molecules.[4] In certain cases, cubic phases are observed at intermediate chain length[5] and hence at intermediate curvature; the building block here is also clearly related to aggregate formation.

The mesomorphism of calamitic (rodlike) mesogens is typically characterized by the formation of nematic and a whole family of smectic phases and interfacial curvature does not normally play a role in explanations of the observed behavior as the interface is planar. For example, smectic phase formation can be accounted for by the microphase separation between the central, more rigid part of the molecules and the flexible terminal chains. Cubic phases are seen here, too, and the first examples were reported by Gray in the late 1950s.[6] Although much more common than they were, cubic phases still remain rather rare and the driving force for their formation is not well understood in the case of calamitic mesogens.[7]

Figure 1. Structure of the Ag(I) stilbazole complexes.

Figure 2. Structure of some tetracatenar metal complexes (labeling of atoms refers to NMR data in ref 17).

Some time ago, we reported on the observation of cubic phases in some formally ionic, calamitic complexes of silver(I) (Figure 1).[8] The phase behavior of these materials is noteworthy because they show nematic,[9] S_A and S_C phases in addition to the cubic phase. Although formally ionic, they are quite tightly ion-paired and so can be considered as mesogens with a lateral chain. Such mesogens show[10] the nematic phase exclusively as the lateral chain precludes association into layered smectic phases. However, if mesogens with lateral chains show *only* nematic phases, then the observation of the S_A and S_C phases in these complexes is surprising. And, how to interpret the formation of the cubic phase? In fact, it is possible to consider arguments in terms of interfacial curvature in which the alkyl sulfate chain plays a role[11] and while these arguments hold to a good degree, the fact that a S_A phase, with a planar interface, exists to high temperature of the cubic phase suggests that this factor is not significant on its own.

Levelut[12] advanced that specific, electrostatic interactions between silver cations and alkyl sulfate anions were important in these systems. These interactions are clearly not too strong (witness the nematic phase at short chain lengths), but in combination with the longer chain length and accompanying microphase separation, they can stabilize the observed smectic phases through intermolecular interactions. But are they important for cubic phase formation?

As well as looking at complexes of *mono*alkoxystilbazoles, we have also examined those derived from 3,4-*di*alkoxystilbazoles (Figure 2) and we have looked at complexes of Pd(II) (**3**) and Pt(II) (**4**)[13] in addition to those of Ag(I) (**2**).[14] Here we make some interesting observations, namely that complexed to silver dodecyl sulfate, these stilbazoles show both cubic and columnar phases, but no smectic phases, while with Pd(II) or Pt(II), S_C and columnar phases were observed, but no cubic phase. Consideration of the structure of these complexes suggests that the principal difference is the presence of the alkyl sulfate chain in the silver materials and, given that in polycatenar mesogens cubic and columnar phase

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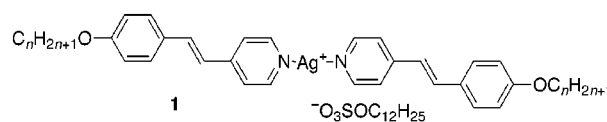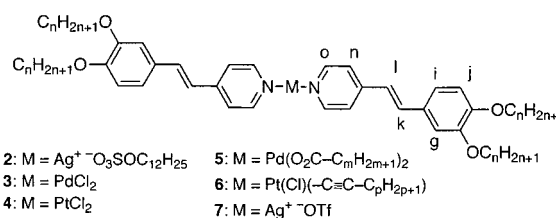(6) Gray, G. W.; Jones, B.; Marson, F. *J. Chem. Soc.* **1957,** 393.

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formation depends on curvature at the interface, we reasoned that if we could add some volume to the core of the palladium complexes, then perhaps we could control the curvature and thereby induce cubic phase formation. We attempted this by making palladium alkanoate complexes of the stilbazoles (**5**) and found to our surprise that whether we employed mono-, di-, or even trialkoxystilbazoles and whatever the chain length, only nematic phases were seen![15] Thus, addition of these chains to the smectogenic complexes did not modify the interface, rather leading to the loss of microphase separation giving a nematic phase. Similarly, addition of the alkanoate chains to columnar-forming complexes might have been expected to reduce curvature and lead to the observation of a cubic phase, rather than the nematic phase found.

However, consideration of the structures of **2** and **5** shows that while the alkanoate chains in the latter may have contributed to the volume of the core, there is no proper structural comparison between the two as one contains two lateral chains while the other contains one. We therefore considered structural types which we might use to realize complexes with only one lateral chain and we decided upon monoalkyne complexes using Pt as the central metal (**6**). We needed to use Pt as unsymmetric complexes of this type would be much less likely to disproportionate, and in any case, the mesomorphic behavior of the Pt complexes (**4**) is very similar to that of the palladium congeners (**3**).

The coupling of the acetylene to the Pt center was carried out with CuI and an amine base, following procedures outlined by Raithby.[16] While, in principle, the synthesis of the complexes is straightforward, we found that care was needed to ensure monosubstitution rather than disubstitution. Short reaction times seemed to offer the necessary control, although it was not possible to define a single, optimum reaction time. Curiously, however, we also found that the *mono*substituted complexes were best formed using a 3-fold excess of the acetylene. The compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and by elemental analysis, all of which were in agreement with the proposed formulation.[17] We were also able to obtain the disubstituted complexes by similar procedures using longer reaction times and 6 equiv of acetylene.

We made a series of these complexes, but for the purposes of this paper we need discuss only two, namely those for which $n = 4$ and 10 with, in each case, $p = 13$. Pentadecyne was chosen as the acetylene as we wished to make a close comparison with the silver complexes where there is a 15-atom lateral chain ($O-S-O-C_{12}H_{25}$). For complex **2** with $n = 4$, only a cubic phase is observed, while when $n = 10$ both a cubic and a columnar phase are seen.[13] However, for **6** with $n = 4$ and $p = 13$, we found a smectic C and a nematic phase (Cr·130·S$_C$·147·N·153· dec); the same mesomorphism was found for $n = 10$ and $p = 13$ (Cr·88·S$_C$·96·N·138·I). For comparison and for the purposes of discussion, it is also relevant to compare the properties of **7** where no mesophase is found for $n = 4$, while a cubic phase only is found for $n = 10$.[18]

Let us begin by recalling that the complexes **3** and **4** behave as classical polycatenar mesogens showing both a S$_C$ and a columnar phase; curiously the cubic phase is absent. However, when we add a single lateral chain and a charged moiety (**2**), we lose the S$_C$ phase, retain the columnar phase, and add the cubic phase; loss of the smectic phase is almost certainly due to the presence of the lateral alkyl sulfate chain. If we add two chains to **3** to produce **5**, then we find only nematic phases. However, in **7** we retain the ionic function (not present in **5**), but lose the lateral chain (although there is little doubt that the triflate anion will be associated closely with the silver cation). Finally, we consider **6** where we have retained a single, lateral chain, but lost the possibility of intermolecular electrostatic interactions and here we find a nematic and a S$_C$ phase.

It has been speculated previously that intermolecular interactions[6,10,19] are important for cubic phase formation in calamitic materials and this is consistent with the structures of the materials which show these phases.[7] However, it is only now with the systematic structural variations which have been possible on account of the presence of a metal center that we can say with confidence that this is the case. Thus, while complexes **6** have a somewhat more restricted geometry than the silver complexes (**1**, **2**, and **7**), we believe that they provide a good structural analogy *minus* the intermolecular electrostatic interactions, and the discovery of a nematic phase rather than a cubic phase supports the importance of these interactions. Of course, we also find that while electrostatic interactions are clearly pivotal in these systems, they are not the only factor of importance, although it does seem that cubic phases are absent without them.[10]

For some time, the factors influencing the formation of this rare phase in calamitic mesogens have been the subject of discussion and we believe that we have produced important evidence for a key factor, namely specific intermolecular interactions. These interactions imply once more that aggregate formation may be significant, suggesting a common factor with the purely polycatenar systems described above.

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(17) Complex **4**[13] ($n = 4$) (1 g, 1.09 mmol) was dissolved in a mixture dichloromethane/diisopropylamine (10/1; 120 mL/12 mL) at room temperature. Subsequent addition of copper(I) iodide (2%, 22 mg) was then followed by addition of 1-pentadecyne (3 equiv, 853 μL). The solution was then allowed to stir at room temperature for 10 min after which the solvents were evaporated and the crude reaction mixture analyzed by ^{1}H NMR spectroscopy to determine the yield (94.5%); traces of the corresponding disubstituted complex were detected. The monosubstituted complex was then purified by column chromatography. A 1/3 ethyl acetate/hexane mixture eluted remaining alkyne and traces of disubstituted complex, while the monosubstituted complex was recovered by eluting with pure ethyl acetate. It was then crystallized from diethyl ether and finally recovered as a yellow solid by centrifugation. δ_H (400 MHz; CDCl$_3$) **6**($n = 4$, $p = 15$): 0.83 (t, $^3J = 6.7$ Hz, 3H), 0.95 (2t, $^3J = 7.4$ Hz, 12H), 1.47 (m, 32H), 1.78 (m, 8H), 2.34 (t, $^3J = 6.8$ Hz, 2H), 3.98 (t, $^3J = 6.6$ Hz, 4H), 4.01 (t, $^3J = 6.6$ Hz, 4H), (t, $^3J = 6.7$ Hz, 3H), 6.79 (l, AB, $J = 16.1$ Hz, 2H), 6.82 (j, d, $J = 6.8$ Hz, 2H), 7.05 (i, dd, $^4J_{ig} = 1.7$ Hz, $^3J_{ij} = 6.8$ Hz, 2H), 7.07 (g, d, $^4J_{gi} = 1.7$ Hz, 2H), 7.21 (n, AA′XX′, $|J_{no} + J_{no'}| = 6.9$ Hz, 4H), 7.27 (k, AB, $^3J_{kl} = 16.1$ Hz, 2H), 8.91 (o, $|J_{nm}+ J_{on'}| = 6.9$ Hz, 4H). δ_C (100 MHz; CDCl$_3$): 13.8, 14.0, 20.9, 28.9, 29.3, 29.4, 29.6, 29.7, 30.6, 31.2, 31.3, 31.9, 22.6, 68.8, 69.1, 69.0, 91.2, 112.0, 113.4, 121.5, 121.6, 122.0, 128.6, 135.8, 146.8, 149.3, 150.7, 153.8. Elemental analysis Calcd (Found): **6**($n = 4$, $p = 15$) C 62.9 (62.9); H 7.5 (7.6); N 2.5 (2.3); **6**($n = 10$, $p = 15$) C 72.3 (72.1); H 9.6 (9.8); N 1.7 (1.5).

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