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Preliminary Communication

Characterisation by X-ray diffraction of the S₄ phase of some silver(I) complexes of alkoxystilbazoles

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The S₄ phase of a complex of silver(I) dodecylsulphate with two alkoxystilbazole ligands has been studied by X-ray scattering. Our preliminary results suggest that the phase has a tetragonal symmetry; the space group has also been identified.

Since it was first identified in laterally substituted biphenylcarboxylic acids, the cubic mesophase has been the subject of much interest, speculation and study. Once rare, it has been identified in an increasing number of systems, and in several cases the space group has been identified. One of the more intriguing aspects of the cubic phase has been the appearance in some samples, and under certain conditions, of a birefringent phase known commonly as the S₄ phase. Being birefringent, it therefore cannot have cubic symmetry, yet it would appear always to occur in conjunction with a cubic phase [1, 2].

It was first suggested, on the basis of its optical texture (formation of bâtonnets and then a mosaic type texture), that the phase could have a columnar structure [1]. Indeed, the optical texture resembled the columnar phase shown by di-isobutylsilanediol. However, owing to its instability, there was no successful characterization of the phase by X-rays, and thus, its structure remained a mystery.

As part of our studies of metal-containing liquid crystals [3], we have carried out a thorough investigation of the mesomorphism of silver(I) complexes of alkoxystilbazoles [4]. A general structure of these complexes is shown in figure 1. These complexes display a rich mesomorphism which is now summarized.

For $Y = Z = H$, all complexes exhibited SmA and SmC mesophases at high temperatures (up to 250°C) for

$X = \text{OTf}$ and NO_3, and at lower temperatures (up to 170°C) for $X = C_m H_{2m+1} OSO_3$. For short chain lengths and with $X = \text{OTf}$ and $C_m H_{2m+1} OSO_3$, the materials also showed a nematic mesophase. However, in many ways the most interesting observation was that for $m \geqslant 12$, many of the complexes showed a cubic mesophase between the SmC and SmA phases. Cubic phases were most commonly observed for $m = 12$, with some being observed for $m = 14$. However, for $m = 8$ and 10 the cubic phase disappeared, being largely replaced by the SmA phase in the phase diagram. Lateral fluorine substitution was found to affect this mesomorphism such that for $X = C_{12}H_{25}OSO_3$, $Y = F$ and $Z = H$ (figure 1), the cubic phase disappeared entirely, while for $X = C_{12}H_{25}OSO_3$, $Y = H$ and $Z = F$, the cubic phase persisted, giving in one case, a new phase sequence, namely I→N→cub, also observed by Yano and co-workers [5]. Polycatenar derivatives were also found to possess a cubic phase, such that for $X = C_{12}H_{25}OSO_3$, $Y = OC_n H_{2n+1}O$ and $Z = H$ (figure 1), cubic phases were observed for smaller values of n. The space group in some of these cubic materials has now been identified

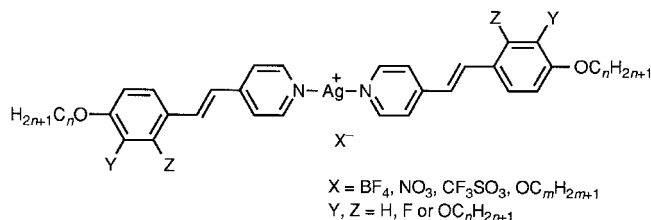X = BF₄, NO₃, CF₃SO₃, OC_mH_{2m+1}
Y, Z = H, F or OC_nH_{2n+1}

Figure 1. Structure of silver salts studied previously.

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as *Ia*3*d* by either X-ray [6] or freeze-fracture electron microscopy experiments [7].

Although absent from the polycatenar derivatives, the S_4 phase was observed in the simpler complexes where $Y = Z = H$. While Demus had been able to assign conditions whereby the S_4 could reproducibly be obtained in the nitrobiphenyl-4-carboxylic acids (see figure 2) [8], we found that the appearance of the S_4 phase was much less predictable in our materials. Thus, on some occasions we might obtain *only* the S_4 phase on heating, whereas on other occasions, it might be entirely absent. This suggests very strongly that transitions between at least the cubic and S_4 phases, and to some degree their surrounding phases, are kinetically rather than thermodynamically driven. Nevertheless, we were on many occasions able to obtain the S_4 phase with a good temporal stability.

The S_4 phase observed in the silver series and in the nitrobiphenyl-4-carboxylic acids appeared between a lamellar (smectic) and a cubic phase, that is the transition between these two phases occurred through an intermediate phase. Similarly, in some lyotropic systems where a cubic phase is inserted between the lamellar and hexagonal phases, the lamellar-to-cubic transition can proceed through an intermediate (hexagonal) step, depending on the kinetics of the phase transformation [9]. In the present case, it seems very likely that the transition between the smectic phases (1D) and the cubic phase (3D) goes through an intermediate structure that is either 2- or 3-dimensional. If thermotropic systems were to be described in terms of surfaces [10] (corresponding to the interface resulting from the segregation between the aromatic and aliphatic parts of the molecules), then a transition between two mesophases might correspond to a change in the topology of this interface. This implies that a phase transition between two adjacent structures does not necessarily involve the total destruction of one structure, but rather preserves and uses elements of each. Therefore, it is possible to analyse the change of topology at the transition by X-ray diffraction, the main probe being the epitaxial relationship between the two mesophases. Furthermore, it is also possible to propose models of phase transitions, 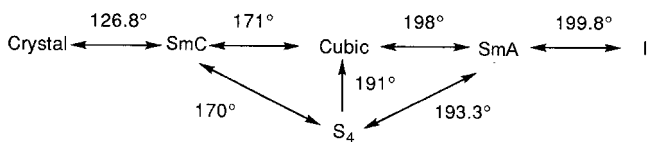as long as they are consistent with these epitaxial relationships [11]. Thus, one can easily imagine that during the smectic-to-cubic transition, the change of topology between the two infinite periodical surfaces associated with both the lamellar and cubic structures would imply a 'transitional structure' with an intermediate surface; this surface would 'template' either the lamellar or the cubic phase formation, in a similar way to some lyotropic systems displaying the lamellar–bicontinuous cubic–hexagonal phase sequence [12].

Given the persistence of the S_4 phase in these complexes and our success in obtaining good X-ray data on the cubic phase, we were encouraged to try to obtain information on the phase. The material chosen for this study had $X = C_{12}H_{25}OSO_3$, $Y = Z = H$, $n = 11$ (figure 1).

For the structural determination of the S_4 phase, we used:

- A Guinier camera, where typical exposures of one hour permitted observation of the two main diffraction lines of the cubic phase (2 1 1 and 2 2 0).
- The synchrotron source at LURE for a complementary investigation; the sample inserted in a Mettler heating stage was heated or cooled at a constant rate (typically 1 K per minute) while the evolution of the diffraction pattern was registered on a time-resolved scale using a CCD camera.

It was thus possible to collect several different patterns with the same sample and to detect the evolution of the powder pattern upon cooling (temperature control ± 1 K). However, we have met some difficulties in performing reproducible experiments due to the following problems:

- As the samples are heated by air flux, the transition temperatures may vary from sample to sample and in addition, the temperature gradient between the point of measurement and the sample can vary quite dramatically.
- A chemical decomposition occurs after long cycles on the same sample.
- The growing process of the S_4 seems to have kinetics that depend on the thermal history of the sample.
- Owing to the large size of the crystals and despite the rotation of the sample, textural effects could not be avoided, resulting in a striated diffraction pattern.

The following results were obtained. On heating, we observed typical patterns of the smectic and cubic phase. The layer thicknesses were found to be 39·1 and 35·5 Å for the SmA and SmC, respectively. The LURE experiments showed the relationship between the layer thicknesses and the size of the structural elements of the cubic

Figure 2. Thermal behaviour of 4′-hexadecyloxy-3′-nitrobiphenyl-4-carboxylic acid after Demus and adapted from reference [7], with limits of superheating and supercooling omitted.

phase. Thus, the SmA layer thickness is equal to the 2 1 1 reticular distance, while the SmC layer thickness is equal to the 2 2 0 reticular distance of the cubic lattice. In fact the 2 1 1 and 2 2 0 reflections of the cubic structure have the highest structure factors. However, as we have obtained neither cubic single crystals nor aligned smectic phases, we were actually not able to establish epitaxial relationships in this case. On cooling, the number of small angle rings varied from one (in the SmA phase) to three rings, and the pure smectic C phase was never recovered at low temperature. Given the experimental difficulties described in the preceding section, some of the patterns obtained showed a mixture of different phases, making their identification non-trivial. However, it appears that among the 18 patterns (corresponding to five different samples) with at least two sharp small angle rings, only two show a mixture with the crystalline phase.

Two or three reticular distances between 40·5 and 33·5 Å were measured and the ratio of the largest spacing to the other(s) is reported in figure 3. In the cubic phase, this ratio must be unique and equal to $2/3^{1/2} = 1·1547$. In figure 3, the points are found on one of three lines, of constant ratio $1·132 \pm 0·009$, $1·155 \pm 0·002$, and $1·1685 \pm 0·003$. Any two points corresponding to the same pattern were always located on the two extreme lines, and therefore we were able to distinguish between a cubic lattice of *Ia3d* symmetry and a tetragonal lattice which corresponds to a slight distortion of the cubic form. In fact, we have never detected a mixture of the two phases.

Since the only modification in the diffraction pattern is a splitting of the 2 2 0 line, the tetragonal space group $I4_1/acd$ is likely. Moreover, assuming that the unique inner ring is the 2 1 1 (rather than the 1 1 2), then the best assignment corresponds to $c > a$ (unique axis *c*); figure 4 shows the lattice constants of the two mesophases. Despite the small number of observed rings, the
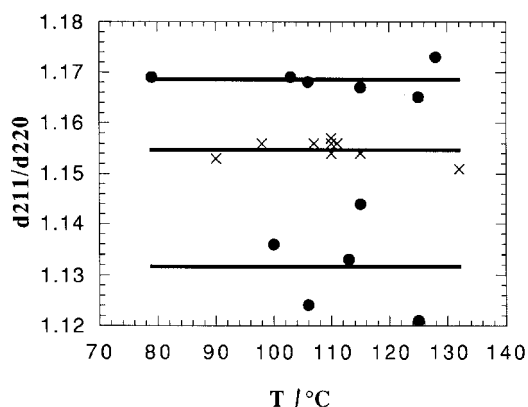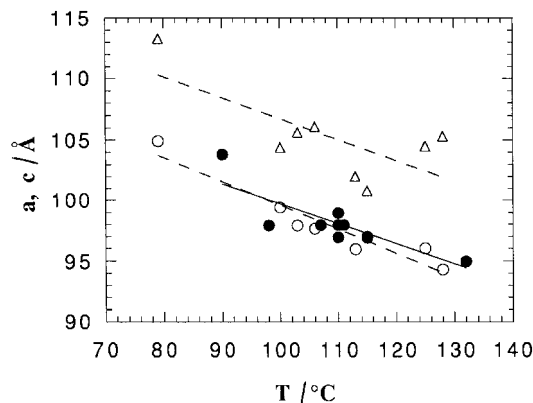

Figure 4. Temperature dependence of the lattice constants of the cubic lattice (full circles) and the tetragonal lattice (open symbols: circles for *a* and triangles for *c*).

points fit reasonably well with a linear dependence versus temperature, justifying our interpretation. However, among the eight patterns we obtained corresponding to the S_4 phase, only three of them showed the doublet, 2 0 2–2 2 0, while two showed only the 2 0 2 line, and the last three the 2 2 0 line; there is no obvious explanation of these observations. The temperature dependence is similar for the two mesophases and moreover the square based edge, *a*, of the tetragonal phase is almost equal to the cubic lattice constant at the same temperature. The unit cell volume increases by about 30% as the temperature decreases from 130 to 80°C. If one assumes that the number of molecules per unit cell increases at the same rate, then the mean area per chain is reduced by 10% when the temperature decreases from 130 to 80°C. Consequently one can estimate that the increment of the mean area per chain is at least of 0·2%/K in the cubic phase, and possibly more if one takes into account the change in molecular volume. This value is slightly higher than the rate of change of the chain area in a SmA phase (0·15% K for TBBA [13]).

In conclusion, therefore, we report the first characterisation by X-rays of the so-called S_4 mesophase, the birefringent companion of the cubic phase of *Ia3d* symmetry. This phase has a three-dimensional tetragonal space group $I4_1/acd$ and therefore the aliphatic end groups of the molecules which are located on an infinite periodic minimal surface in the cubic phase [9] are now located on a slightly distorted IPMS. However, there are still some unresolved problems concerning the specific or general character of the S_4 phase:

- Is there a unique relationship between the texture and the structure of this metastable phase?
- Can this phase transform into a cubic phase with a symmetry other than *Ia3d*?

Figure 3. Ratio of the largest measured reticular spacing to the others; X = mean value of $2/3^{1/2}$ corresponding to a cubic lattice, ● = ratios for a tetragonal lattice.

- What is the relationship between the S_4 phase and the SmQ phase [14]?

We are on the way to answer some of these three questions. The so-called SmQ phase is another example of a mesophase with tetragonal symmetry. In fact, under the SmQ label, one can distinguish four different space groups [15], three of which are tetragonal ($I4_122$, $P4_122$ and $I4$) and one of which is hexagonal ($P6_222$). However, the interfaces between the molecular layers are strongly twisted in these mesophases. Nevertheless they are closely related to the cubic $Ia3d$ phase. The binary phase diagram of a chiral molecule with its racemic mixture exhibits three mesophases, the SmQ ($I4$) phase on the side of the pure enantiomer, and the $Ia3d$ and $I4_1/acd$ mesophases, coexisting on the racemic side [15]. A direct transition between the same SmQ ($I4$) phase and the cubic $Ia3d$ was found in a binary mixture of a chiral molecule with 4'-hexadecyloxy-3'-nitrobiphenyl-4-carboxylic acid [14]. The problem of the relationship between the texture and the structures of metastable phases surrounding cubic mesophases of different symmetry, will be developed in another paper [16].

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