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**To cite this Article** Fletcher, I. D. , Guillon, D. , Heinrich, B. , Omenat, A. and Serrano, J. L.(1997) 'The stabilization of smectic A phases in mixtures of twinned-calamitic, metal organic complexes with 2,4,7-trinitro-9-fluorenone', Liquid Crystals, 23: 1, 51 — 58

**To link to this Article: DOI:** 10.1080/026782997208668

**URL:** http://dx.doi.org/10.1080/026782997208668

LIQUID CRYSTALS, 1997, VOL. 23, NO. 1, 51–58

# The stabilization of smectic A phases in mixtures of twinned-calamitic, metal organic complexes with 2,4,7-trinitro-9-fluorenone

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(*Received 23 January 1997; accepted 19 March 1997*)

The liquid crystal properties of binary mixtures of copper- and palladium-containing, twinned-calamitic, metal organic complexes with the electron acceptor 2,4,7-trinitro-9-fluorenone (TNF) are reported. The smectic A to isotropic transition temperature of the pure metal organic component is increased on mixing. Furthermore, only smectic A behaviour is exhibited by the mixtures compared with smectic A and C phases for the pure metal organic complexes. The stabilization of the smectic A phase in these mixtures is found to be due to a weak charge transfer type interaction.

## 1. Introduction

The induction and stabilization of liquid crystal phases resulting from mixtures of electron-rich and electron-deficient materials is an area of burgeoning interest. It has been shown, for example, that a mixture of the disc-shaped material, pentakis(phenylethynyl)phenyl nonyl ether, with the electron acceptor TNF (both of which are non-liquid crystalline) gives rise to an induced discotic phase and the newly discovered columnar nematic phase [1]. Stabilization of liquid crystal phases is also known in mixtures of TNF with polymers containing side chain discotic units [2], disc-shaped, palladium- [3] and platinum-containing [4] organometallic complexes and more recently hexacatenar materials [5]. The occurrence of such liquid crystal behaviour is thought to result from the formation of an electron donor–acceptor complex, as indicated by a yellow-to-deep red colour change on mixing the compounds, which is stabilized through charge transfer interactions [6]. However, it is also possible that other factors such as quadrupolar interactions between groups with quadrupole moments which are opposite in sign could also be responsible for favourable interactions necessary for mesophase induction in the mixture. Furthermore, an increase in entropy resulting from a mixture of the two components may also help to stabilize liquid crystal phases [7]. A more complete overview on the induction and stabilization of mesophases by the interaction between flat molecules with aromatic cores and organic electron acceptors is outlined in reference [8]. In the field of metal-organyl mesogens, several systems have been studied, most of them exhibiting a disc-shaped molecular structure. In these cases, on doping with TNF, columnar mesophases are stabilized. Moreover, lyotropic mesophases are also observed in mixtures with apolar organic solvents [8]. Metal organic complexes with an almost linear humpbacked molecular shape which do not show mesomorphic behaviour in the pure state give rise to columnar mesophases when mixed with TNF [9].

In the present work, we wished to further the fundamental understanding of such binary mixtures and for this reason we present here results obtained from mixtures of copper- and palladium-containing, twinned-calamitic, metal organic complexes with TNF (see the structures in figure 1).

The molecular shape of these complexes is also almost linear and they show smectic mesophases in the pure state. When mixed with TNF, the stabilization of the smectic A mesophase occurs. No induction of columnar mesophases has been observed. We also wished to examine the effect of electron density on the liquid crystal properties of the mixtures and for this reason we have chosen two different metal centres.

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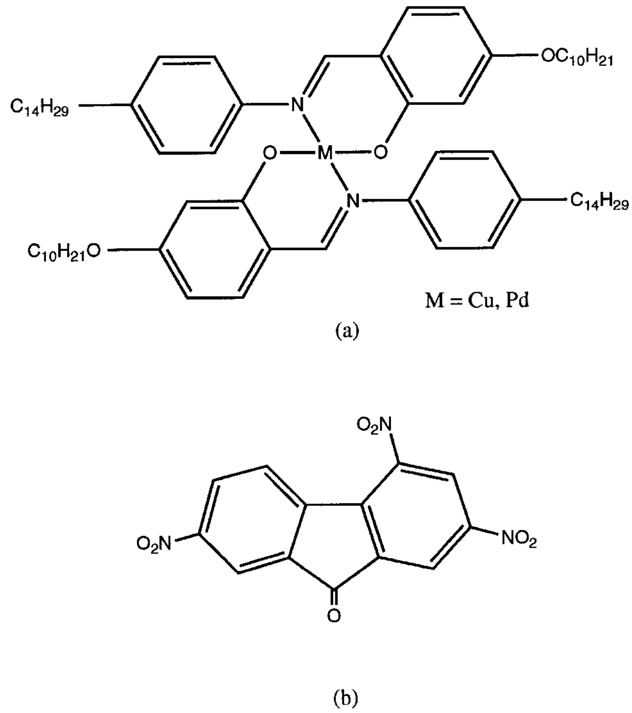


Figure 1. The molecular structures of (*a*) the metal-containing complexes ($M$ = Cu, Pd) and (*b*) TNF.

## 2. Experimental

The preparation of the light brown copper derivative followed the experimental methods outlined in reference [8], and its characterization was consistent with that expected for its structure. The palladium compound was obtained by a similar method as a yellow powder in a yield of 83% using palladium acetate as the metal source. Its structural characterization is as follows: melting behaviour, Cr (161·5°C SmC) 163·0°C SmA 164·5°C I; elemental analysis with calculated values in parentheses, C 73·79% (73·82%), H 9·93% (9·64%), N 2·31% (2·33%); $^1$H NMR (Varian XL-200 200 MHz), $\delta$ (ppm) 0·9 (t, 6H), 1·2–1·4 (m, 34H), 1·6–1·7 (m, 6H), 2·6 (t, 2H), 3·7 (t, 2H), 5·5 (d, 1H), 7·2 (m, 4H), 7·6 (s, 1H); IR (Perkin-Elmer 1600 series FTIR) KBr disc, $\nu$ (cm$^{-1}$) 1636 (CH–N).

Mixtures of the complexes with TNF were obtained by melting together weighed amounts of the two components. The thermal properties of the mixtures were characterized by differential scanning calorimetry (Perkin-Elmer DSC7); polarizing optical microscopy (Olympus BH-2 microscope), in conjunction with a Linkam TMS90 hot stage, was used to identify the nature of the liquid crystal behaviour. X-ray diffraction patterns of the liquid crystal phases of the pure samples and their equimolar mixtures with TNF were obtained with two experimental set-ups. In the first technique, diffraction patterns were obtained by employing linear monochromatic Cu-$K_{\alpha 1}$ radiation obtained from a sealed tube generator and a bent quartz monochromator and the patterns were recorded with an Inel CPS 120 counter. The samples were filled into Lindemann capillaries and their temperature controlled within ±0·05°C. In the second method, Cu-$K_{\alpha 1}$ radiation was obtained by means of a nickel filter and the diffraction patterns were registered on photographic films. The samples were again filled into Lindemann capillaries and their temperature controlled within ±0·3°C. The experimental error in the layer spacings of the smectic phases was less than 0·2 Å over the entire range measured.

Electrochemical measurements of the pure metal organic complexes were performed with an EG and G Princeton Applied Research Model 273 potentiostat system coupled to a plotter. A cell fitted with three electrodes consisting of a platinum wire working electrode, a standard calomel reference electrode (SCE) and a counter electrode was employed. The metal organic complex and 0·1 M of the electrolyte tetrabutylammonium hexafluorophosphate were dissolved in dry dichloromethane under a nitrogen atmosphere. All potentials are referred to versus the SCE. A potential of − 1·6 to + 1·6 V was used with a sweep rate of 20 m V s$^{-1}$. UV-vis (Uvikon 941) measurements on the metal organic complexes, TNF and their mixtures were carried out using dry tetrahydrofuran solutions.

## 3. Results and discussion

A contact preparation between the copper complex and TNF gave an orange band at the junction of the two components (see figure 2(*a*)). The contact preparation shown in figure 2(*a*) is at room temperature, since in the mesophase the coloured band is not so clearly seen, and shows that both the contact region and the pure organic complex cool into an amorphous state. The colour change in the contact region between the two phases has been observed before in mixtures with TNF and is thought to be due to the formation of an electron donor–acceptor complex stabilized through a charge transfer interaction.

Figure 3 shows the phase diagram for the two component system and table 1 lists the corresponding data. As can be seen, all compositions exhibit a smectic A phase as determined by polarizing optical microscopy, which was characterized by the coexistence of focal-conic fan and homeotropic textures. A monotropic smectic C phase was also identified by microscopy for the mixture containing 90 mol % of the copper complex and exhibits both the broken focal-conic fan and schlieren textures. The smectic A to isotropic transition temperature reaches a maximum for the 50 : 50 mol % composition which is also the eutectic point for the phase diagram and indicates that a complex between

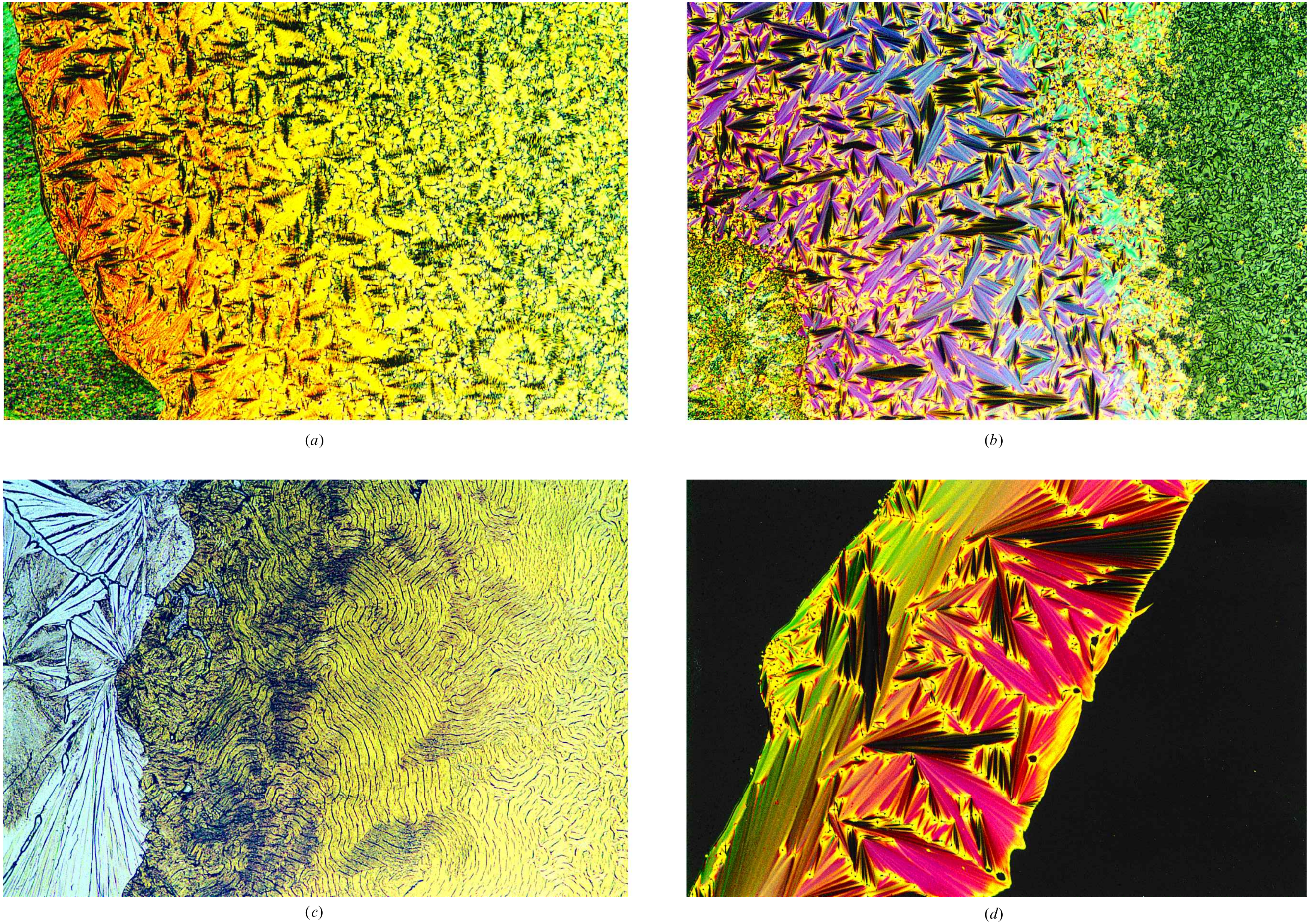


Figure 2. Microphotographs for the contact preparations between the metal-organic complex and TNF. All preparations are at magnification of ×75 and exhibit the following phase order from left-to-right: (*a*) crystalline TNF/amorphous orange charge transfer band in the contact region/amorphous pure copper-containing complex at room temperature; (*b*) crystalline TNF/smectic A phase of contact region/smectic C phase of pure copper-containing complex at 126°C; (*c*) crystalline TNF/amorphous dark charge transfer band in the contact region/amorphous pure palladium-containing complex as viewed without crossed polarizers at room temperature; (*d*) isotropic TNF/smectic A phase of the contact region/isotropic pure palladium-containing complex at 181°C.

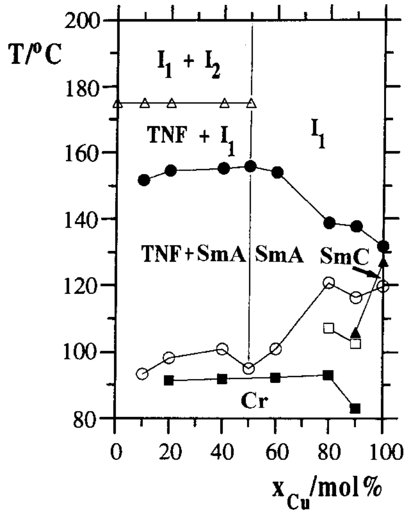


Figure 3. The phase diagram for the copper complex/TNF binary system. ■ Cr$_1$–; □ Cr$_2$–Cr; ○ Cr–; ▲ SmC–SmA; ● SmA–I; △ Cr$_{TNF}$–I.

the two components has formed which has a 1:1 stoichiometry. For the 10 to 50 mol% mixtures, unmixed crystalline TNF is also present and at temperatures greater than 175°C the immiscible isotropic phases of the mixture ($I_1$) and of TNF ($I_2$) coexist. From the phase diagram it is seen that the smectic C phase formed by the pure copper compound is quickly extinguished on adding TNF and is only monotropic for the 90 mol% copper composition. This behaviour suggests that the TNF molecules are favourably accommodated in the smectic A phase structure, which results in an increase in phase stability. Figure 2(*b*) clearly demonstrates the switchover from smectic C to smectic A behaviour on mixing the metal organic complex with TNF.

A contact preparation between the palladium compound and TNF showed a dark brown band at the junction of the two phases when the sample was viewed without crossed polarizers (when viewing with crossed polarizers a very slight colour change was seen in the contact region) and indicates charge transfer behaviour (see figure 2(*c*)). Again it is seen from the figure that both the contact region and the pure metal organic complex cool into an amorphous state. Figure 4 presents the phase diagram for the binary system and table 2 presents the data for these compositions.

The liquid crystal phase behaviour for the mixtures is similar to that for the copper complex/TNF system with again smectic A and C phases being exhibited and the equimolar composition being the stoichiometric mixture. Unmixed TNF is also present for mixtures containing 10 to 50 mol% palladium composition. The smectic A to isotropic transition temperatures are, however, higher than those of the copper complex/TNF system and this observation is consistent with the difference in the clearing temperatures of the pure samples. Indeed, for the contact region, the smectic A to isotropic transition temperature occurs above the clearing temperatures of the pure components as is clearly seen in figure 2(*d*). However, it appears that increasing the electron density of the metal does not have a big effect on the stability

Table 1. The transition temperatures (°C) and transition enthalpies (kJ mol$^{-1}$; in italics) for the copper-containing mixtures with TNF.

| $x_{Cu}$/mol % | Cr$_1$ | | Cr$_2$ | | Cr | | SmC | | SmA | | I |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | | | | | ● | 93·3<br>*8·94* | | | ● | 151·7<br>*1·33* | ● |
| 20 | ● | 91·3<br>*28·47*$^{a}$ | | | ● | 98·3 | | | ● | 154·6<br>*6·97* | ● |
| 40 | ● | 91·8<br>*48·43*$^{a}$ | | | ● | 101·0 | | | ● | 155·3<br>*7·67* | ● |
| 50 | | | | | ● | 95·0<br>*51·50* | | | ● | 156·0<br>*7·69* | ● |
| 60 | ● | 92·3<br>*75·87*$^{a}$ | | | ● | 101·0 | | | ● | 154·1<br>*8·70* | ● |
| 80 | ● | 93·0<br>*21·00*$^{b}$ | ● | 107·3 | ● | 120·7 | | | ● | 133·3<br>*8·61* | ● |
| 90 | ● | 83·0<br>*59·72*$^{d}$ | ● | 102·6 | ● | 116·3<br>*18·13* | (● | 106·0$^{c}$)$^{e}$ | ● | 137·7<br>*12·16* | ● |
| 100 | | | | | ● | 119·6<br>*35·27* | ● | 127·2<br>*0·36* | ● | 131·7<br>*13·26* | ● |

[a] For a Cr$_1$–Cr–SmA transition as peaks are overlapped.
[b] For a Cr$_1$–Cr$_2$–Cr–SmA transition as peaks are overlapped.
[c] Only observed by polarizing microscopy.
[d] For a Cr$_1$–Cr$_2$–Cr transition as peaks are overlapped.
[e] Brackets indicate a monotropic transition.

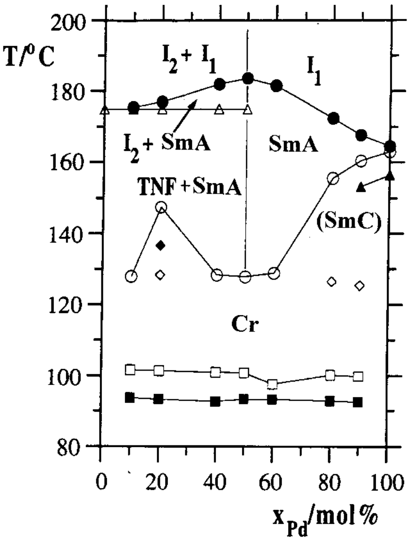


Figure 4. The phase diagram for the palladium complex/TNF binary system. ■ $Cr_1$–$Cr_2$; □ $Cr_2$–; ◇ $Cr_3$–; ◆ $Cr_4$–Cr; ○ Cr–SmA; ▲ SmC–SmA; ● SmA–I; △ $Cr_{TNF}$–I.

of the smectic A phase in the mixture with TNF, although we might have expected a more electron-rich metal to be more easily oxidized and therefore have a stronger electronic interaction with TNF than a metal with a lower electron density.

Tables 1 and 2 also list the transition enthalpies for the smectic A to isotropic transitions of the copper- and palladium-containing mixtures, respectively. Interestingly, for both systems the transition enthalpy decreases as the mol fraction of TNF increases. Such behaviour has also been observed for discotic systems [11, 12].

Electrochemical analysis by cyclic voltammetry of the redox behaviour of the pure complexes shows that the metal organic complexes do not undergo oxidation and that weak reduction occurs which is not reversible. For the copper complex, a weak reduction process occurs with a peak potential of +0·73 V and a peak current of 100 mA. The cyclic voltammogram for the palladium complex gives two small peaks on the reduction cycle, one with a potential of +0·62 V (peak current=12 mA) and one with a potential of −0·1 V (peak current= 20 mA). This evidence, together with the UV-vis spectroscopy [13] experiments which failed to show the presence of new electronic bands in addition to those detected for the components in their pure states, and IR spectroscopy [14] of the mixtures in which the vibrational frequencies of the stretching modes of the nitro groups of TNF are not seen to move (a normal consequence of charge transfer), supports the weak charge transfer behaviour observed by microscopic studies.

The structure of the smectic A phases exhibited by pure samples of the metal-containing complexes and by equimolar mixtures of the complexes with TNF were examined by X-ray diffraction. Figures 5(*a*) and 5(*b*) show the X-ray diffraction patterns obtained with the Inel CPS 120 counter during monitoring of the liquid crystal behaviour of the pure copper-containing sample and its equimolar mixture with TNF, respectively. Figures 6(*a*) and 6(*b*) show the corresponding patterns for the palladium-containing samples. (In the case of figure 6(*b*) some tiny peaks are observed in the wide angle region due to a small amount of undissolved crystalline TNF). The occurrence of higher X-ray reflections in the small angle region of figures 5(*b*) and 6(*b*) is evident in the case of the mixtures compared with the pure complexes, and implies that the addition of TNF improves the stacking in the layers, resulting presumably from a better segregation of aliphatic chain and hard core regions in adjacent sub-layers. Within the hard cores' sub-layer, the packing is disordered for the pure compounds and for the mixtures, as shown by the

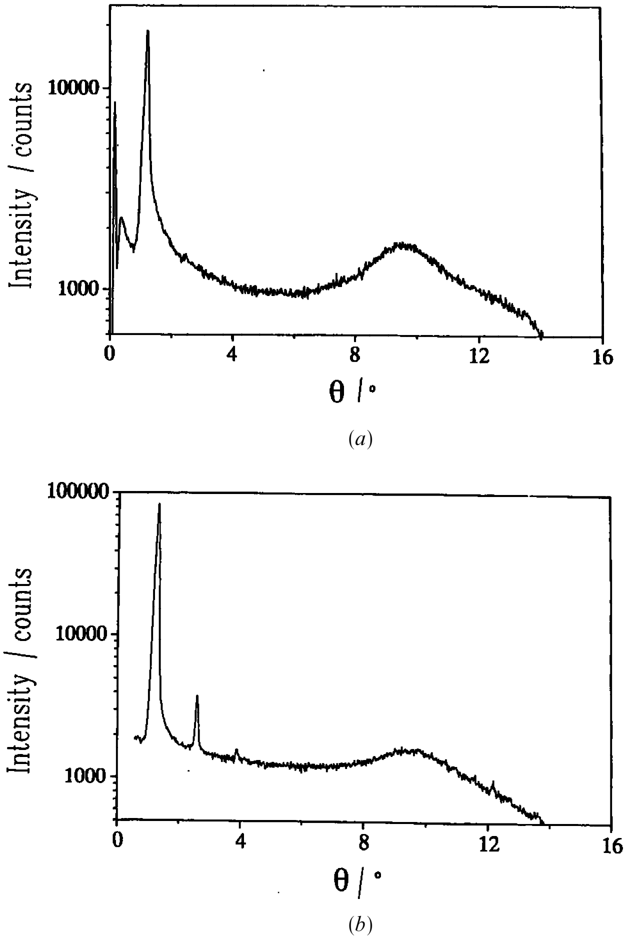
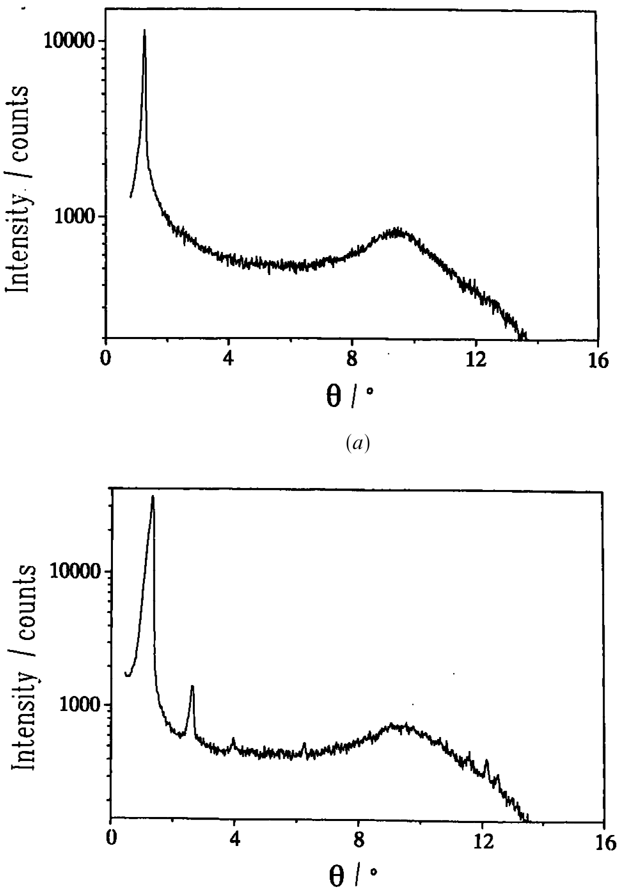


Figure 5. X-ray diffraction patterns for the smectic A phase of (*a*) the pure copper complex at 131°C and (*b*) its equimolar mixture with TNF at 110°C.

Table 2. The transition temperatures (°C) and transition enthalpies (kJ mol$^{-1}$; in italics) for the palladium-containing mixtures with TNF.

| $x_{Pd}$/mol % | $Cr_1$ | | $Cr_2$ | | $Cr_3$ | | $Cr_4$ | | Cr | | SmC | | SmA | | I |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | ● | 93·7<br>*1·02*[a] | ● | 101·7 | | | | | ● | 128·0<br>*3·33* | | | ● | 175·5<br>*0·75* | ● |
| 20 | ● | 93·3<br>*2·07*[a] | ● | 101·4 | ● | 128·4<br>*6·44* | ● | 136·6<br>*0·08* | ● | 147·5<br>*0·90* | | | ● | 177·0<br>*1·80* | ● |
| 40 | ● | 92·7<br>*6·73*[a] | ● | 101·0 | | | | | ● | 128·4<br>*19·68* | | | ● | 181·9<br>*4·72* | ● |
| 50 | ● | 93·3<br>*6·32*[a] | ● | 100·9 | | | | | ● | 127·9<br>*24·64* | | | ● | 183·6<br>*6·95* | ● |
| 60 | ● | 93·3<br>*5·22*[b] | ● | 97·7 | | | | | ● | 128·9<br>*17·58* | | | ● | 181·4<br>*8·05* | ● |
| 80 | ● | 92·9<br>*6·70*[a] | ● | 100·3 | ● | 127·1<br>*9·08* | | | ● | 155·6<br>*20·74* | | | ● | 172·5<br>*9·41* | ● |
| 90 | ● | 92·6<br>*8·07*[a] | ● | 99·9 | ● | 125·2<br>*2·66* | | | ● | 160·5<br>*32·09* | (● | 153·3[c])[f] | ● | 167·7<br>*9·85* | ● |
| 100 | | | | | | | | | ● | 163·0<br>*56·78*[d] | (● | 161·5)[f]<br>*0·89* | ● | 164·5<br>*9·74*[e] | ● |

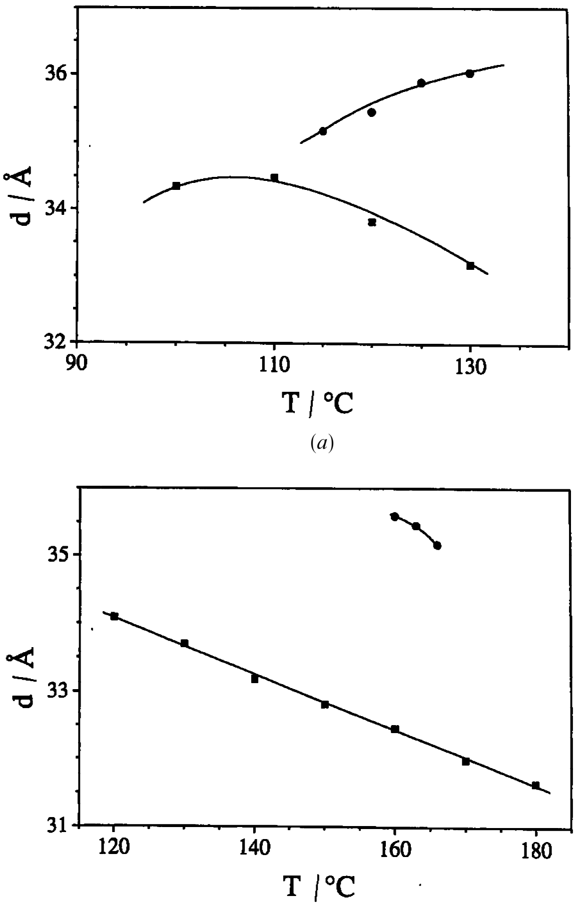
[a] For a $Cr_1$–$Cr_2$–Cr transition as the peaks are overlapped.
[b] For a $Cr_1$–$Cr_2$–$Cr_3$–Cr transition as the peaks are overlapped.
[c] Only observed by polarizing microscopy.
[d] Cr–I transition.
[e] Value taken from DSC cooling scan.
[f] Brackets indicate a monotropic transition.



(*a*)

(*b*)

Figure 6. X-ray diffraction patterns for the smectic A phase of (*a*) the pure palladium complex at 166°C and (*b*) its equimolar mixture with TNF at 140°C.



(*a*)

(*b*)

Figure 7. The effect of temperature on the layer periodicity for (*a*) the copper-containing complex (●, pure sample; ■, equimolar mixture with TNF), (*b*) the palladium-containing complex (●, pure sample; ■, equimolar mixture with TNF).

broad diffuse reflection in the wide angle region. On adding TNF, changes from tilted to untilted phases (observed for both complexes) are not surprising, since they reflect the disturbance of the long range correlated positional and bond ordering between the hard cores due to the intercalation of the molecules. Another consequence of the addition of TNF is the larger mean distance between the hard cores of the metal organic complexes and the larger area covered by one alkyl chain. The aliphatic sub-layer has to be thinner, therefore, and the overall layer thickness smaller (the molecular length of the metal complexes in their all *trans*-form is 43 Å as calculated from a Dreiding molecular model) (see figure 8). This is clearly observed in figures 7(*a*) and 7(*b*) for the copper- and palladium-containing samples, respectively. The temperature dependence of the layer thickness is also classical [15], with a small decrease with increasing temperature in the smectic A phase, due to enhanced conformational disorder in the alkyl chains, while in the smectic C phase an increase in the tilt angle leads to a decrease in the layer thickness.

Figure 8 gives two schematic representations of the possible structure of the smectic A phase exhibited by mixtures of the metal-containing complexes and TNF. In one, the TNF molecules are accommodated in a regular fashion between the metal-containing complexes. The resulting space could be filled by an intercalation of the flexible alkyl chains of the metal-containing complexes in adjacent sub-layers causing a reduced layer periodicity (see figure 8(*a*)). In the other representation, the space arising could be occupied by the alkyl chains of the metal-containing complexes in the same layer which again would lead to a reduced layer periodicity (see figure 8(*b*)). However, in this model the chains would need to possess *gauche* links to allow the chains to occupy the vacant space.

The investigation by X-ray diffraction of the effect of

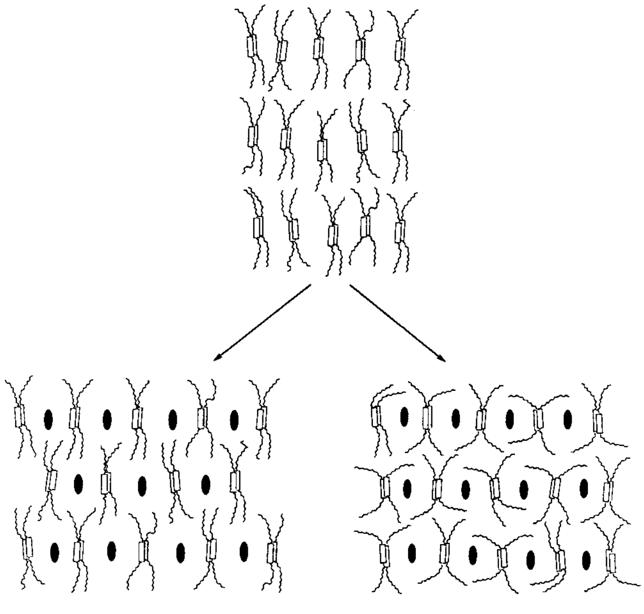


Figure 8. The possible molecular arrangements for a stabilized smectic A phase produced by an equimolar mixture between the metal-containing molecules and TNF (shown in black): (*a*) a reduction in the layer periodicity resulting from an intercalation of the alkyl chains of metal-containing complexes in neighbouring layers; (*b*) a reduction of the layer periodicity as a consequence of the alkyl chains of metal-containing complexes in the same layer filling empty space.

adding TNF to these metal-containing complexes has revealed that the segregation of aliphatic chains and hard cores in adjacent sub-layers is improved, which is consistent with the observed stabilization of the smectic A domain. This suggests strongly that the addition of TNF enhances the intermolecular interactions within the hard cores' sub-layer and is consistent with the observation of charge transfer behaviour as observed from polarizing microscopy studies.

## 4. Conclusions

The results presented in this work have shown that a weak charge transfer interaction exists for the mixtures of these metal-containing complexes with TNF. Furthermore, X-ray analysis of the metal complexes and their mixtures with TNF indicates that the segregation of hard cores and aliphatic chains in adjacent sub-layers is improved when TNF is added. However, unlike mixtures of discotic materials with TNF, in which dramatic changes occur, such as the induction and the stabilization of liquid crystal phases to more than 100°C above the clearing temperature of the pure discogen, here modest increases of about 25°C are observed, although the phase range is increased considerably.

We wish to acknowledge the European Commission for the award of a Human Capital and Mobility individual fellowship (No. ERBCHB1CT941157) to Dr I. D. Fletcher, and the European Network ERBCHRX-CTP3-U161.

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