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# ALKYL- AND ALKOXY- AROYLHYDRAZINATO METAL COMPLEXES - UNUSUAL X-RAY DIFFRACTION WITHIN THE SMECTIC C PHASE.

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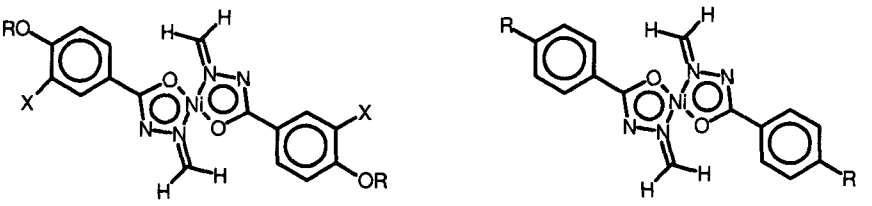
Abstract Two homologous series of novel nickel containing liquid crystalline complexes have been synthesised [1-3]. The effect of changing chain length and chain type on phase behaviour is reported here. Optical microscopy, DSC and x-ray scattering is used to identify the phase structures. X-ray scattering from the smectic C phase shows unusual diffraction patterns with the intermolecular scattering larger than would be expected.

## INTRODUCTION

Metal containing liquid crystals, or metallomesogens, are important because they may have novel practical applications. The inclusion of a metal centre into a mesogen can impart colour, enhanced polarisability and magnetic properties [4,5] which can lead to faster switching devices and coloured displays without the need for guest/host dye systems. They also provide the opportunity to study metal complexes in a highly ordered organic environment.

The liquid crystals studied here are alkyl- and alkoxy- arylhydrazinatonickel(II) complexes, figure 1. The alkyl- complexes showed smectic A (SmA) phases only, identified by their optical textures. The alkoxy- complexes showed nematic phases (N) at short chain length and smectic C (SmC) phases at longer chain length, figure 2. The schlieren textures from these latter two phases could be distinguished by their viscosity and by the number of brushes associated with the texture. The nematic schlieren texture exhibits point singularities with two and four brushes; the SmC schlieren four only.




Alkoxy complex Alkyl complex

FIGURE 1 Alkyl- and alkoxy- arylhydrazinatonickel(II) complexes. The X on the alkoxy- complex is H or F.

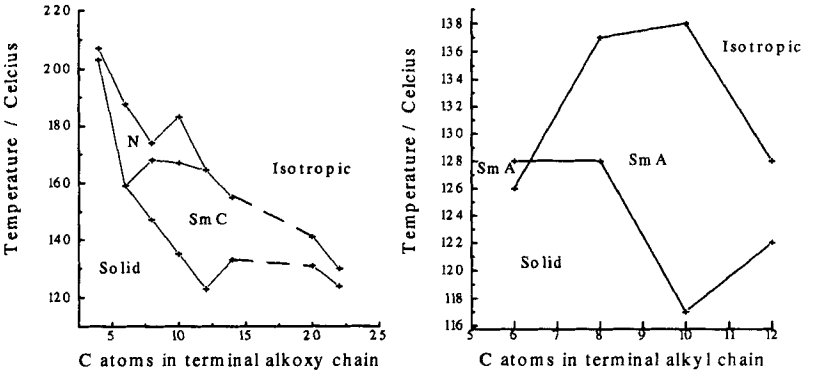



FIGURE 2 Phase diagrams of the alkoxy- and alkyl- hydrazinatonickel(II) complexes.

## X-RAY DIFFRACTION

The x-ray diffraction patterns from unaligned smectic A samples of the alkyl chain compounds show diffuse reflections at (0.45±0.05) nm, corresponding to the alkyl chain spacing and a sharp layer reflection line at (3.1±0.1), (3.5±0.1) and (3.8±0.1) nm for the $C_8$, $C_{10}$ and $C_{12}$ compounds respectively. X-ray scattering patterns from the unaligned smectic C phases of the R=$OC_{22}$ and R=$OC_{14}$ complexes are shown in figures 3a and 3b. Each shows two outer diffuse rings at (0.45±0.05) nm and (1.8±0.2) nm for both samples and one sharp inner ring at (5.1±0.1) nm for R=$OC_{22}$ and (4.4±0.1) nm for R=$OC_{14}$ respectively. The latter rings are from the layer spacing because there is a well defined second order in the ratio of 1:2 in each case. Once again the reflection at 0.45 nm is the inter-alkyl chain reflection. The layer spacing in the alkoxy chain system is

comparable or slightly smaller than those measured in the equivalent alkyl chain molecules, taking into account the additional oxygens in the chain.

Fluorination at position X in the alkoxy system gives a system which may be readily aligned in the smectic C phase by both surfaces and by an applied magnetic field. This presumably arises because of the dipole moment associated with the fluorine. Figure 4 shows the scattering pattern from the 3-fluorinated $OC_{14}$ compound cooled from the

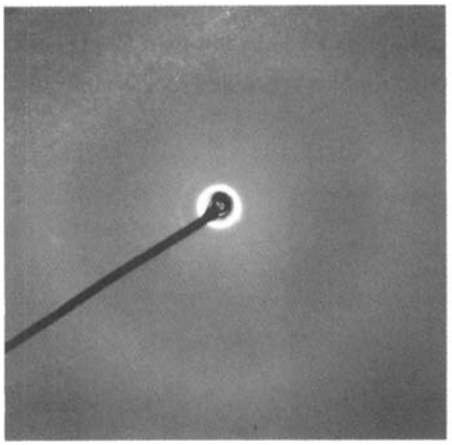


FIGURE 3a Unaligned R=$OC_{22}$ SmC phase.

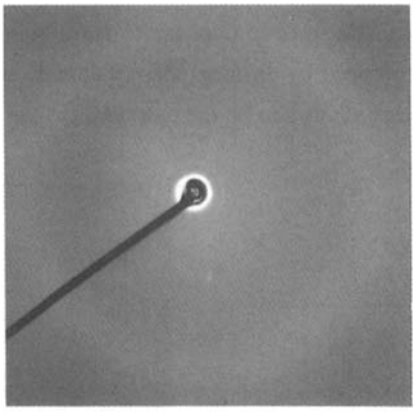


FIGURE 3b Unaligned R=$OC_{14}$ SmC phase.

isotropic phase in a magnetic field of 0.5T in the direction shown. As expected there is a reinforcement of the layer reflection along the field direction, indicating a positive molecular anisotropy of the diamagnetic susceptibility. The layer spacing is identical to its hydgrogenated counterpart. Both the 0.45nm and 1.8 nm reflections are also present although the former is weaker (an effect of the shorter exposure for an aligned sample) and the latter also shows some reinforcement in the direction perpendicular to the magnetic field and the plane normal. Thus the 1.8 nm reflection appears to be associated with the molecular spacing between the aromatic cores. A simple calculation from the molecular geometry shows that the separation of two nickel ions in adjacent molecules will be of the order of circa 0.9 nm, about half the x-ray measured spacing.

## DISCUSSION AND CONCLUSIONS

Two intriguing questions are posed by the results reported here. First, why the replacement of alkyl by alkoxy chains should favour the formation of smectic C rather

than smectic A phases and second, why the molecular separation in the smectic layer is apparently twice the molecular width? We would expect the x-ray scattering in a smectic C phase to show two features[6,7] - the interlamellar scattering and a broad feature determined by the molecular width, not twice that width. We speculate that the answer to both these questions may be answered by the presence of the alkoxy oxygen and its association with the N- methylidene moity on the central core. For the first question, a similar effect is noted for alkyl- and alkoxy- substituted azobenzenes[8], with the tendency for the smectic C phase to form being increasingly favoured as terminal alkyl chains are replaced by terminal alkoxy chains, and outboard dipoles are added to the molecule. We assume this to be the case here.

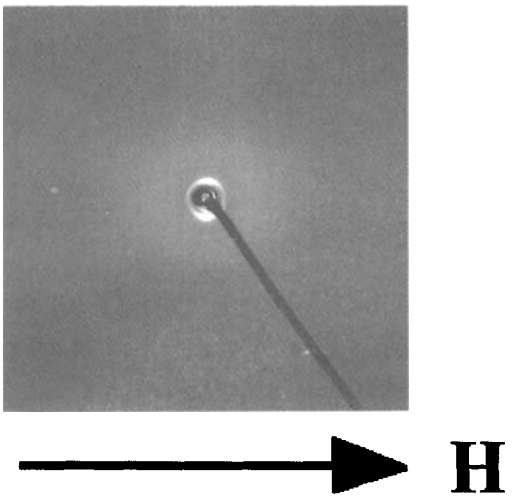



FIGURE 4 X-ray scattering from the 3-fluorinated R=OC14 complex. The magnetic field is in the direction indicated.

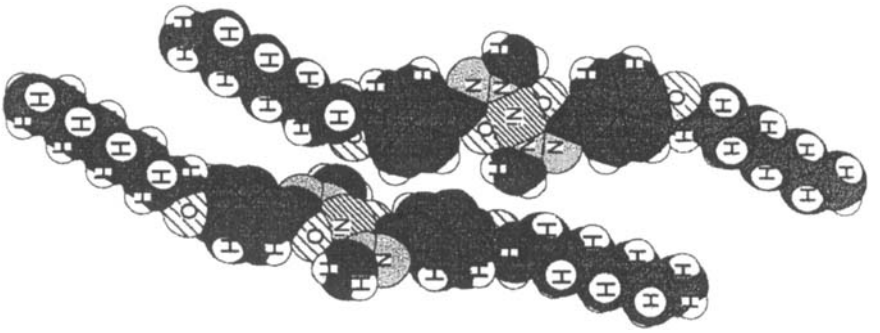


Figure 5 A schematic representation of the association of neighbouring alkoxy molecules within the smectic C phase.

Perhaps more speculative is the explanation for why the separation is apparently twice the molecular width. With the addition of the oxygen the molecules form a temporary association with their neighbours; in this way the planar complexes containing the nickel centre make an angle of ca. 130° determined by the oxygen lone pair electrons and the N- methylidene moity, as in figure 5. Using this and the approximate width of the nickel square planar complex, gives a separation between first nearest neighbour molecules with the same orientation of circa 1.9 nm, close to the observed distance. Thus although the molecules do rotate about their long molecular axes, there is sufficient association between neighbouring molecules to be able to distinguish between them - ie. adjacent molecules are not spatially identical.

A more detailed account of optical microscopy, DSC and x-ray scattering measurements on this system is in preparation.

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