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## Liquid Crystals

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### Nematic and smectic mesophases in a new series of Cu(II) organometallic complexes

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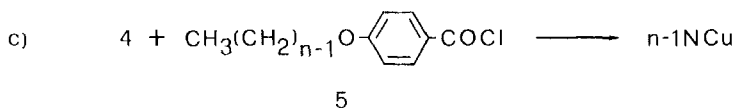
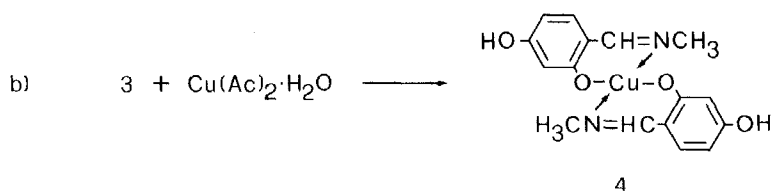
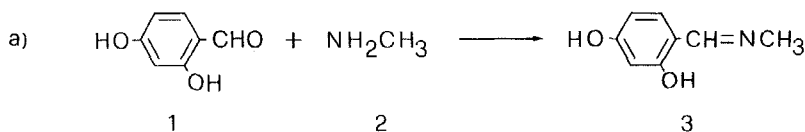
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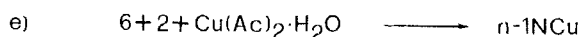
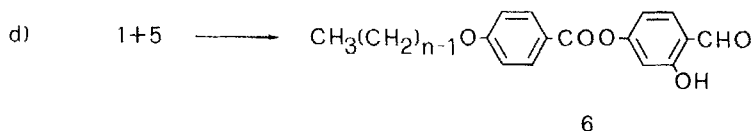
The chemical formula was designed with the purpose of favouring the onset of nematic mesomorphism by enhancing the molecular linearity with respect to the smectogenic copper, bis[4-[[[4-(alkoxy)-2-hydroxyphenyl]methylene]amino]alkoxyphenyl] complexes [9] and their *n*-alkanoyloxy homologues [10]. Actually, with the exception of a single compound, all of them exhibit nematic mesomorphism and some of them are also smectogenic. The molecular core which has been utilized is highly versatile. In a forthcoming article we shall describe the influence exerted on the mesophasic behaviour by longer aliphatic chains connected to the nitrogen atoms. The mesophasic properties of polymers whose linear structure is obtained by enchainment either via the nitrogen atom or via the *p*-oxygen atom of the salicyl group are also under scrutiny.

## 2. Experimental

For reasons which we shall indicate the chemical synthesis was performed following two different procedures whose steps are outlined in the scheme:



Scheme A



Scheme B

Procedure A: compounds with  $n = 7, 10, 14$

Step (a). Imine 3, *N*-[(2,4-dihydroxyphenyl)methylene]methanimine, precipitates by reaction of gaseous methylamine bubbled in large excess in a diethylether solution of 2,4-dihydroxybenzaldehyde. The imine was used, after solvent evaporation, without any purification. The  $^1\text{H}$  N.M.R. spectrum of a sample purified by successive crystallization is consistent with the formula. Thermal decomposition starts at 460 K without melting.

Step (b). Imine **3** dissolved in 95 per cent ethanol and copper acetate was then added. The solution was boiled for 5 min; brown coloured **4**, copper, bis[*N*-[(2,4-dihydroxyphenyl)methylene]methanamino], separates on cooling. It was purified by crystallization from a solution in a 85/15 vol. of dimethylsulphoxide-water mixture. Thermal decomposition without melting starts at 570 K. Copper content as CuO: 21.86 per cent calculated; 21.68 per cent found.

Step (c). The synthesis of 7-1NCu, copper, bis[*N*-[[4-[(heptyloxy)benzoyloxy]-2-hydroxyphenyl]methylene]methanamino], is reported as an example. 0.620 g of **4** were dissolved in a 100 ml water solution containing 0.247 g KOH and 2.0 g benzyltriethylammoniumchloride. To this solution, was added a 40 ml chloroform solution containing 0.910 g of compound **5** ( $n = 7$ ) while stirring rapidly. The mixture was left to react for about eight minutes, then 50 ml chloroform were added and the total chloroform phase was separated, washed with water, dried over sodium sulphate and concentrated to half the volume by evaporation. To this solution 130 ml hot 95 per cent ethanol were added and, by successive cooling at about  $-15^{\circ}\text{C}$ , 7-1NCu separates as brown-green crystals (yield: 40 per cent). The copper complex was purified by crystallization from ethanol/chloroform solution, successive column chromatography (Florisil, chloroform as eluent) and finally crystallization. Copper content as CuO: 10.80 per cent calculated; 10.70 per cent found.

Procedure B: all compounds:

The synthesis of 10-1NCu is described as an example.

Step (d). At room temperature 50 ml of a dioxane solution containing 5.940 g of compound **5** ( $n = 10$ ) were added dropwise during 30 min to a solution containing 2.764 g of compound **1** and 2.1 ml pyridine in 100 ml dioxane. The reaction mixture was then brought to the boiling temperature and cooled by pouring it into 1 l freezing water. The precipitate was crystallized from 95 per cent ethanol solution. Pure **6**, 4-[4-(decyloxy)benzoyloxy]-2-hydroxybenzaldehyde (m.p. 354.5 K), was obtained by repeated crystallization from ethanol solution. The final  $^1\text{H}$  N.M.R. spectrum was consistent with the formula.

Step (e). 0.5 ml of a 35 per cent (weight) water solution of methylamine were added at room temperature to 40 mL of a 5/3 (vol) dioxane/95 per cent ethanol mixture containing 0.573 g of **6** ( $n = 10$ ). The temperature was then brought to  $60^{\circ}\text{C}$  and 0.144 g of copper acetate added. The complex precipitates as large brown crystals on cooling the solution. Yield 40 per cent. The purification is described at step (c). Copper content as CuO: 8.99 per cent calculated; 9.04 per cent found.

The imine corresponding to compound **6**, *N*-[[4-[4-(alkoxy)benzoyloxy]-2-hydroxyphenyl]methylene]methanamine, was prepared and isolated only for  $n = 10$ . This was done with a procedure similar to that described at step (a). The compound, whose  $^1\text{H}$  N.M.R. spectrum was consistent with the formula, melts to a nematic liquid at 345.5 K and starts to form the isotropic phase and thermally decomposes at 368.2 K.

The synthesis of the carboxylic acids corresponding to compounds **5** was performed with standard procedures from alkylbromides and 4-hydroxy, methylbenzoate. Their phase behaviour is consistent with literature data [11].

These copper complexes which were prepared following both procedures have indistinguishable behaviour. The reason for developing two procedures, however, is not connected to the opportunity of cross-checking their results but to their different versatility. Procedure A appears more suitable for the preparation of homologous series of compounds which preserve the same intermediate salicylaldiminate group, such as **4**, whatever the inserted amine may be. The same holds for the synthesis of

polymers, e.g., polyesters, if the enchainment is obtained by use of the *p*-hydroxy groups of the same intermediate compounds. Procedure *B* is more convenient for the synthesis of homologous series when molecular group **6** is kept constant and the amine group to be inserted is the one varied.

For the thermal characterization of all compounds a DSC-2 Perkin Elmer apparatus calibrated with a high purity indium sample was used. The DSC curves were recorded under dry nitrogen flow with a 10 K/min scanning rate. The optical observation of the phase behaviour was performed utilizing a Leitz polarizing microscope with a Mettler FP5 temperature controller. For further investigating of the nature of the mesophases, CuK $\alpha$  X-ray diffraction spectra were recorded at the appropriate temperature with a flat-film camera. The <sup>1</sup>H N.M.R. spectra were recorded on a 270 MHz Bruker spectrometer. Selected data concerning some key compounds are reported at table I.

Table I. Selected <sup>1</sup>H N.M.R. data ( $\delta$ ) for three organic ligands taken as a reference. I = *N*-[(2,4-dihydroxyphenyl)methylene]-methanamine; II = 4-[4-(decyloxy)benzoyloxy]-2-hydroxy-benzaldehyde; III = *N*-[[4-[4-(decyloxy)benzoyloxy]-2-hydroxyphenyl]methylene]methanamine. Abbreviations: d = doublet; d\* = pseudodoublet, actually forming a AA'XX' multiplet; t = triplet; no attribute = singlet;  $-\Phi-$  = phenyl ring. Number in parentheses for hydrogen atoms of I refer to the position in the ring. Solvent: deuteriated chloroform for II and III, deuteriated dimethylsulphoxide for I (the presence of a small amount of H<sub>2</sub>O prevented the detection of  $-\Phi-OH$  resonances for this compound)

I		II		III	
$-\Phi-H(3)$	6.10 d	$-\text{O}(\text{R})-\text{CH}_3$	0.90 t	$-\text{O}(\text{R})-\text{CH}_3$	0.89 t
$-\Phi-H(5)$	6.20 d*	$-\text{CH}_2-\text{O}-\Phi-$	4.06 t	$-\text{CH}_2-\text{O}-\Phi-$	4.05 t
$-\Phi-H(6)$	7.12 d	$-\Phi-OH$	11.25	$-\Phi-OH$	13.91
$-\Phi-CH=N$	8.30	$-\Phi-CHO$	9.89	$-\Phi-CH=N$	8.34
$=N-CH_3$	3.32			$=N-CH_3$	3.49

### 3. Results and discussion

All of the copper complexes which have been examined exhibit enantiotropic liquid-crystalline behaviour. Tables 2 and 3 report some relevant data concerning the phase transitions. An overview of the phase behaviour is given in figure 1.

With the exception of 14-1NCu the nematic phase has been constantly observed. It has been recognized systematically by the appearance of a very mobile schlieren texture at the onset of optical anisotropy on cooling the isotropic liquid. Figure 2 shows the nematic schlieren pattern for 11-1NCu at 484 K. Further confirmation was obtained for the same compound by recording the X-ray diffraction pattern at 480 K. Apart from the usual wide angle halo no Bragg diffraction signal corresponding to any smectic periodicity, at least within 60 Å, was detected. The nematic range, which is almost independent of the length of the alkoxy groups when it is the only mesophase exhibited, undergoes a drastic and progressive decrease when smectic mesomorphism also appears. With 14-1NCu only the smectic phase was observed.

The liquid crystal polymorphism was easily detected by calorimetry, polarizing microscopy and X-ray diffraction techniques. Figure 3 shows the DSC curves for 12-1NCu as an example. The low temperature endothermic signal corresponds to a

Table 2. Phase transition temperature measured at the onset of the DSC endothermic signals for solution crystallized samples.  $\sigma T/T = 0.001$ .  $n$  = number of carbon atoms in the alkoxy terminal chain;  $T_{C_1C_2}$  = solid phase transition;  $T_{C_2S_C}$ ,  $T_{C_2N}$  = melting temperature;  $T_{S_CN}$  = smectic C - nematic transition;  $T_{S_CI}$ ,  $T_{NI}$  = liquid crystal isotropic transition temperature.  $d$  = smectic periodicity measured at temperature  $T$ ;  $\sigma d/d = 0.015$ ,  $\sigma T/T = 0.006$ .

$n$	$T_{C_1C_2}/K$	$T_{C_2S_C}/K$ $T_{C_2N}/K$	$T_{S_CN}/K$	$T_{S_CI}/K$ $T_{NI}/K$	$d/\text{\AA}$	$T/K$
6		484.7		539.1		
7		474.2		525.7		
8		472.1		515.6		
9		459.4		505.9		
10	446.4	452.8	456.9	498.4	—	—
11	429.1	449.0	468.7	491.1	39.1	460
12	425.2	446.7	475.1	486.1	39.7	465
13	422.5	444.1	478.2	481.3	41.7	468
14†	414.4	440.8		477.3	43.3	468

† An additional solid–solid phase transition at 343.6 K.

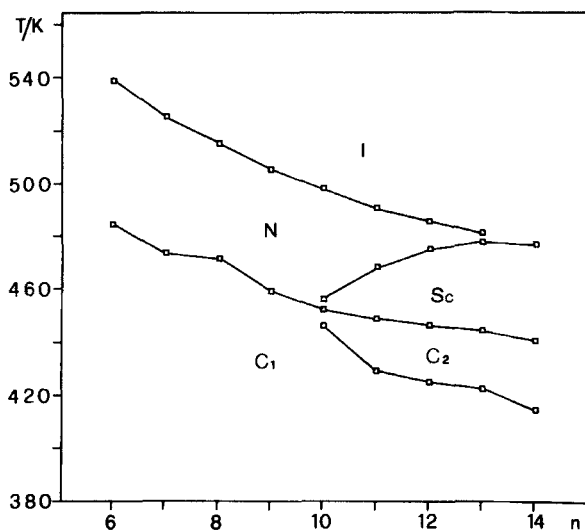


Figure 1. Phase transition temperatures as a function of the number of carbon atoms contained in each alkoxy group. For  $n = 14$  a solid–solid phase transition at 343.6 K is not reported.

solid phase transition. This feature, which is common to all of the smectogenic complexes, will be discussed briefly later on. The successive endotherms are relative to melting, smectic-nematic and isotropic transition, respectively. At the cooling rate of 10 K/min the solid phase transition is not completely reversible. However, complete recrystallization occurs by short annealing or even during the next heating run.

The optical textures observed are indicative of smectic C mesomorphism in all cases. The schlieren and fan type textures were those most commonly observed. Frequently both of them were detectable together. Figure 4 shows a significant texture

Table 3. Enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) changes at the phase transition. DSC data measured for the first heating run of solution crystallized samples.  $0.05 \geq \sigma \Delta H / \Delta H \geq 0.01$ ;  $0.05 \geq \sigma \Delta S / \Delta S \geq 0.01$ .

$n$	$\Delta H_{C_1C_2} /$ $J g^{-1}$	$\Delta S_{C_1C_2} /$ $JK^{-1} mol^{-1}$	$\Delta H_{C_2SC(N)} /$ $J g^{-1}$	$\Delta S_{C_2SC(N)} /$ $JK^{-1} mol^{-1}$	$\Delta H_{SC(N)} /$ $J g^{-1}$	$\Delta S_{SC(N)} /$ $JK^{-1} mol^{-1}$	$\Delta H_{SC(N)} /$ $J g^{-1}$	$\Delta S_{SC(N)} /$ $JK^{-1} mol^{-1}$
6			75.1	120			3.72	5.32
7			69.8	118			3.28	4.97
8			79.1	139			3.27	5.26
9			77.0	144			2.90	4.91
10	36.4	72.2	35.6	69.5	0.71	1.37	2.87	5.09
11	49.0	104	28.8	58.6	1.07	2.10	2.98	5.54
12	48.7	108	27.5	58.1	1.72	3.41	3.39	6.56
13	55.6	128	26.6	58.0	3.60	7.30	4.80	9.65
14†	54.0	130	24.2	54.7			8.86	18.6

† For the additional solid-solid phase transition:  $\Delta H = 14.0 J g^{-1}$ ,  $\Delta S = 40.6 J mol^{-1} K^{-1}$ .



Figure 2. 11-INCu:  $T = 484$  K; nematic schlieren texture. Crossed polarizers.

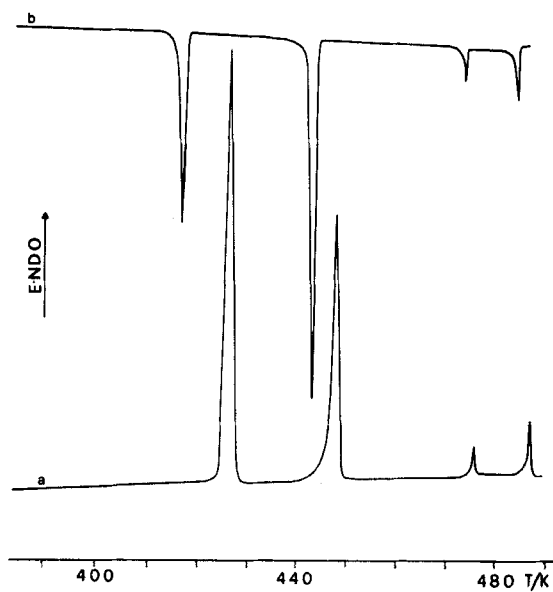


Figure 3. 12-INCu: DSC curves. First heating run for a solution crystallized sample (a); cooling run (b). Scanning rate 10 K/min.



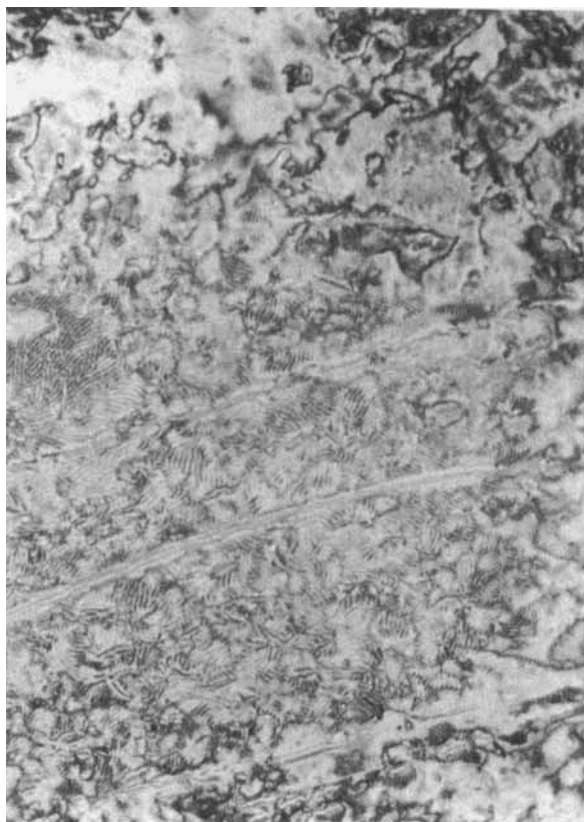


Figure 4. 11-1NCu:  $T = 466$  K; smectic C phase. Schlieren texture with transition bars observed during a cooling run. Crossed polarizers.

containing a smectic C schlieren pattern with transition bars observed for 11-1NCu at 466 K at the transition from the nematic phase with moderate supercooling.

To allow a more direct comparison of the measured smectic periodicities in case they depend on temperature, the X-ray diffraction patterns of 11-1NCu, 12-1NCu, 13-1NCu and 14-1NCu were recorded at a temperature,  $T$ , correspondent to a constant value of  $T/T_1$  ( $T_1$  = smectic-nematic transition temperature; isotropization temperature for 14-1NCu). They are characterized at small angles by a single sharp Bragg diffraction signal. The corresponding lattice distances are reported in table 2.

At variance with a commonly observed feature, melting and isotropic temperatures do not show any significant odd-even fluctuation. They decrease fairly smoothly with increasing length of the alkoxy terminals in such a way that the thermal stability interval of the liquid crystal state is scarcely dependent on that parameter ( $-2.2$  K per added methylene group, on average).

Isotropic enthalpies and entropies take almost constant values up to 11-1NCu with an odd-even fluctuation which is on the border of statistical significance. They increase significantly with the length of the alkoxy terminal chains only for the upper three members of the series.

Although the peculiarity of the molecular core makes any comparison of questionable significance, it may be worth noticing that the isotropic enthalpies per unit mass

are rather low in respect to those available in the literature and concerning low molar mass organic mesogens containing symmetrically linked alkoxy terminals of appropriate length; e.g. [12, 13]. The same is true, although to a lesser extent, for the molar entropic changes. At our knowledge, very few thermodynamic data concerning other metallorganic nematogens are available in the literature. Maitlis *et al.* [5] report a  $2.2 \text{ J g}^{-1}$  value for the nematic-isotropic transition enthalpy of a nematic mixture of two square-planar palladium mesogenic complexes containing 4-alkyl-4'-cyanobicyclohexyl ligands. The value of  $2.0 \text{ J g}^{-1}$  is reported by Ovchinnikov *et al.* [4] for a copper(II) benzaldiminate complex and as low a value as  $0.2 \text{ J g}^{-1}$  is found by Serrano *et al.* [6] for the single nematogenic compound out of a numerous set of mesogenic dinuclear ortopalladate Schiff bases. Finally, an isotropization enthalpy of  $0.38 \text{ J g}^{-1}$  was measured by Chandrasekhar *et al.* [7] for three nematogenic copper, bis[1-(6-decylbiphenyl)-3-(4-alkoxyphenyl)propane-1,3-dionato] complexes. More experimental data are necessary to decide whether the seemingly systematic lowering of nematic-isotropic transition enthalpy is a more general feature calling for adequate explanation.

The solid state behaviour of the compounds reported in this article needs a concise discussion. The relevant thermodynamic data which are reported in tables 2 and 3 refer to samples previously crystallized from solution. The behaviour of melt-crystallized samples is more complicated but it has no influence on the mesophases and, therefore, we shall not discuss it in any detail. The occurrence of a solid phase transition has been observed for solution crystallized samples of the smectogenic compounds; 14-1NCu shows two of them. The total melting enthalpy,  $\Delta H_{\text{mt}}$  (i.e.  $\Delta H_{\text{mt}} = \Delta H_{\text{m}}$  for the compounds with a single solid phase;  $\Delta H_{\text{mt}} = \Delta H_{\text{k}} + \Delta H_{\text{m}}$  for those showing solid polymorphism), is scarcely and irregularly dependent on the length of the alkoxy terminal chains, it is significantly higher than the average value only for 14-1NCu. In contrast, for those compounds showing more than one solid phase, the melting enthalpy  $\Delta H_{\text{m}}$  is drastically reduced (for 14-1NCu it is only 26% of  $\Delta H_{\text{mt}}$ ), regularly decreasing with increasing length of the alkoxy terminal chains.

The crystalline nature of the phase preceding the smectic has been confirmed by X-ray diffraction analysis for 13-1NCu and 14-1NCu. For the former compound the X-ray diffraction pattern recorded at 433 K is unmistakably typical of a crystal phase with sharp diffraction lines up to  $2\theta = 32^\circ$ . A sharp and intense small angle signal corresponding to a  $34.3 \text{ \AA}$  lattice distance is presumably correlated to the packing of the molecular layers that give the smectic structure. Analogous results have been obtained for 14-1NCu. The diffraction spectra were collected at 428 K, 373 K and 295 K. All of them contain, in addition to sharp wide angle signals, an intense small angle Bragg peak corresponding to lattice distances of  $35.7 \text{ \AA}$ ,  $34.5 \text{ \AA}$  and  $33.5 \text{ \AA}$ , respectively.

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