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Nematic and smectic mesophases in a new series of Cu(II) metallorganic complexes. II

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Nematic and smectic mesophases in a new series of Cu(II) metallorganic complexes. II

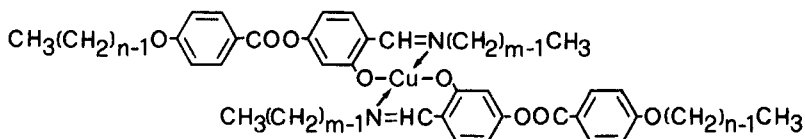
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The synthesis and phase behaviour of a set of copper, bis-[*N*-[[4-[4-(tetradecyloxy)benzoyloxy],2-hydroxyphenyl]methylene]-alkanamino] complexes (referred to as 14-*m*NCu where *m* = 2-14 is the number of carbon atoms in the alkanamino group) is reported. With the single exception of the complex formed with the ethanamine, they show liquid crystal properties, either nematic only (*m* = 3-9) or smectic only (*m* = 15) or both of them (*m* = 10-14). Smectic mesomorphism is of the C type in all cases. The smectic interlayer spacing has been measured for compounds with *m* = 14 and 15 by X-ray diffraction. For both compounds it is significantly shorter than that found previously for *m* = 1. This should indicate that, in spite of the smectic phase homology, some substantial change in the molecular packing has occurred. Most compounds exhibit solid phase polymorphism, which is discussed briefly.

1. Introduction

We have studied the mesomorphic properties of a set of copper, bis[*N*-[[4-[4-(alkoxy)benzoyloxy],2-hydroxyphenyl]-methylene]alkanamino] complexes:

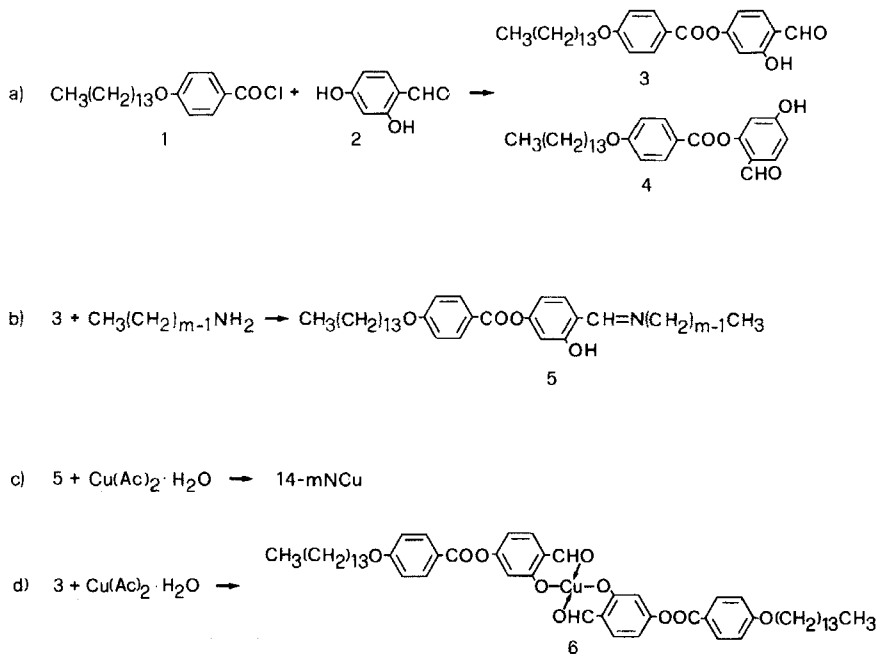


From a preliminary analysis it became apparent that not only were the isotropization temperatures and enthalpies but also the very nature of the mesophase was dependent on the length of both alkoxy and alkanamino groups. A detailed description of the influence of the alkoxy terminal chains has been reported for a homologous series containing the methanamine (*m* = 1) group [1]. Only nematic mesomorphism is shown up to *n* = 9. Both smectic and nematic mesomorphism occur for $9 < n < 14$, with a decreasing nematic stability for increasing *n*, while only the smectic phase is observed for *n* = 14.

In this article we report the mesophasic properties of a homologous series of complexes containing alkanamino groups of increasing length (*m* = 2-15). The tetradecyloxy (*n* = 14) group was used for the alkoxy terminal chains. The reason for making this choice was that of investigating the effects on the mesophasic properties caused by increasing the length of the alkanamino groups of a molecular structure (*n* = 14; *m* = 1) which had proved to be smectogenic itself.

2. Experimental

Copper, bis[*N*-[[4-[4-(tetradecyloxy)benzoyloxy],2-hydroxyphenyl]-methylene]alk-*n*-amino] complexes (14-*m*NCu), were prepared according to a procedure which was described in [1] as procedure B. The essential steps are outlined here. Of the two constitutional isomers which are possible for the imine compounds, only isomer **5** can act as a chelating agent for Cu(II). This made any preliminary separation of isomer **3** and of the corresponding imine from the reaction products unnecessary. The only necessary operation was the separation of unreacted **2** at step a. This was achieved by crystallization of the reaction products from a 95 per cent ethanol solution; **2** which is very soluble does not crystallize. Copper complexes precipitate at step c on cooling the reaction mixture. They were purified by crystallization from ethanol/chloroform solution, successive column chromatography (Florisil, chloroform as eluent) and finally by crystallization from ethanol/chloroform solution. Complexes 14-8NCu and 14-13NCu were also prepared from the previously separated isomer **3** and the corresponding imines **5** ($m = 8, 13$).



Among the possible reaction products of step a, isomer **3** is the only one capable of producing a stable copper(II) complex. This feature was used to isolate pure **3**. The reaction products of step a (previously crystallized from 95 per cent ethanol solution to eliminate unreacted **2**) were dissolved in boiling 95 per cent ethanol. A hot 95 per cent ethanol solution containing a stoichiometric excess of copper(II) acetate was added. Compound **6**, copper, bis[4-[4-(tetradecyloxy)benzoyloxy],2-hydroxybenzaldehydato], precipitated as green platelets. The quantitative analysis of the copper content (as CuO) gave the following result: 8.19 per cent calc., 8.24 per cent found. Compound **6** melts at 510 K with chemical decomposition; two more phase transitions, at 408 K and 438 K, are also detectable by D.S.C.

Table 1. Selected ^1H N.M.R. data (δ ppm) for three organic ligands taken as a reference. **3** = 4-[4-(tetradecyloxy)benzoyloxy]-2-hydroxybenzaldehyd; $5(m = 8)$ = *N*-[[4-[4-(tetradecyloxy)-benzoyloxy]-2-hydroxyphenyl]methylene]octanamine; $5(m = 13)$ = *N*-[[4-[4-(tetradecyloxy)benzoyloxy]-2-hydroxyphenyl]methylene]tridecanamine. Reference numbers are those of scheme 1. Abbreviations: t = triplet; no attribute = singlet; $-\Phi-$ = phenyl ring. Solvent: deuteriated chloroform.

3		$5(m = 8)$		$5(m = 13)$	
$-\text{O}(\text{R})-\text{CH}_3$	0.88 t	$-\text{O}(\text{R})-\text{CH}_3$	0.88 t	$-\text{O}(\text{R})-\text{CH}_3$	0.88 t
$-\text{CH}_2-\text{O}-\Phi-$	4.04 t	$-\text{CH}_2-\text{O}-\Phi-$	4.04 t	$-\text{CH}_2-\text{O}-\Phi-$	4.04 t
$-\Phi-\text{CHO}$	9.88	$=\text{N}-\text{CH}_2-$	3.58 t	$=\text{N}-\text{CH}_2-$	3.58 t
$-\Phi-\text{OH}$	11.25	$-\Phi-\text{CH}=\text{N}$	8.31	$-\Phi-\text{CH}=\text{N}$	8.31
		$-\Phi-\text{OH}$	14.10	$-\Phi-\text{OH}$	14.10

Pure **3** is obtained by reaction of an aqueous solution of hydrogen chloride with **6** in ethanol suspension at 40°C . It melts to an isotropic liquid at 355.0 K . The ^1H N.M.R. spectrum (the significant resonances are reported in table 1) is consistent with the formula. [Incidentally, it is worth noting that the procedure followed to isolate compound **3** shows that esterification of the phenolic function at the ortho position does take place. A substantial amount of 2,4-di-[4-(tetradecyloxy)benzoyloxy]benzaldehyde was separated (melting at 344 K) and identified by ^1H N.M.R.].

The corresponding imines **5** ($m = 8, 13$) were obtained by reaction of the appropriate alkanamine with **3** in hot ethanol solution; they separate as yellow crystals on cooling. A second recrystallization from ethanol solution was performed. The ^1H N.M.R. spectra are in accord with the formula for both compounds, the significant resonances are reported in table 1. Both compounds are mesogenic. Imine **5** ($m = 8$) melts at 342.0 K to a smectic C mesophase which transforms to a nematic phase at 346.7 K and the isotropic phase occurs at 350.6 K . Imine **5** ($m = 13$) melts at 347.0 K to a smectic C phase which becomes isotropic at 358.5 K .

Complexes $14-8\text{NCu}$ and $14-13\text{NCu}$ were synthesized by reaction of the corresponding imines **5** with a hot solution of copper(II) acetate in an equivolumetric dioxane-95 per cent ethanol mixture. The complexes were purified by crystallization from ethanol-chloroform solution, successive column chromatography (Florisil-chloroform) and finally crystallization. Copper content as CuO : $14-8\text{NCu}$ 6.67 per cent calculated, 6.68 per cent found; $14-13\text{NCu}$ 7.17 per cent calculated, 7.18 per cent found.

The phase behaviour of all compounds was investigated by differential scanning calorimetry (D.S.C.-2 Perkin Elmer apparatus, 10 K/min scanning rate) and polarizing microscopy (Mettler FP5 temperature regulator). Smectic structural periodicities were measured for $14-14\text{NCu}$ and $14-15\text{NCu}$ from $\text{CuK}\alpha$ X-ray diffraction spectra recorded photographically on a flat-film camera at the appropriate temperature. $^1\text{H-N.M.R}$ spectra were recorded on a 270 MHz Bruker spectrometer.

3. Results and discussion

Thermodynamic data relevant for discussing the mesomorphic properties are reported in table 2. A simplified form of the phase behaviour is shown in figure 1. If compared to the fairly regular variation of the phase behaviour which was observed for the homologous series $n-1\text{NCu}$ [1] as a function of the length of the flexible terminal chains, some remarkably peculiar features become apparent. The most

Table 2. Phase transition temperatures measured at the onset of the D.S.C. endothermic signal. $\sigma T/T = 0.001$ for four figures values, 0.005 for the others. m = number of carbon atoms in the alkanamine group; $T_{m(sc)}$ = melting of the solution crystallized solid; $T_{m(sc)}$ = melting of the melt crystallized solid; $T_{S_{C-N}}$ = smectic C-nematic transition temperature; T_{Ni} = nematic-isotropic transition temperature for $2 < m < 15$, $T_{S_{C-I}}$ = smectic C-isotropic transition temperature for $m = 1, 15$. Enthalpy (ΔH) changes at the phase transitions. Data concerning solid phase transitions and melting were obtained for the first heating run of solution crystallized samples. The errors in the enthalpies are $0.05 \geq \sigma \Delta H / \Delta H \geq 0.01$

m	$T_{m(sc)}/K$	$T_{m(sc)}/K$	$\Delta H_m/kJ\ mol^{-1}$	$T_{S_{C-N}}/K$	$\Delta H_{S_{C-N}}/kJ\ mol^{-1}$	T_{Ni}/K $T_{S_{C-I}}/K$	$\Delta H_f/kJ\ mol^{-1}$
1(a)	440.8		24.1			477.3	8.83
2	432.8		83.6				
3(b)	408.4	408.4	71.5			422.8	2.37
4	398.5	399.2	114.6			398.5	2.21
5	386.3	385	112.0			401.7	2.26
6(c)	379.4	379.4, 384	(d)			401.2	2.30
7	373.4, 384.6	384.6	(e)			403.1	2.37
8	373	373	119.2			395.9	2.41
9(f)	373, 379.5	373, 379.5	(e)			398.5	2.88
10(f)	380.4	377, 380.4	77.0	370		397.0	3.12
11	386.4	386.4	81.1	381.0	4.94	398.0	3.56
12(g)	382-383	382-383 (g)	81.1	386.6	7.09	396.6	3.84
13	385.1	385.1	77.1	392.0	9.44	397.1	4.33
14	383.3	383.3	71.9	394.3		395.5 (h)	17.4
15	384.4		78.4			396.5	20.1

(a) solid phase transition at 343.6 K and at 414.4 K ($\Delta H = 53.9\ kJ\ mol^{-1}$); data taken from [1]. (b) solid phase transition at 379 K ($\Delta H = 40.3\ kJ\ mol^{-1}$); (c) the high temperature melting solid forms from the low melting one. (d) not properly measurable because recrystallization to a second solid phase takes place during melting. (e) not properly measurable because two different solid phases are present with an unknown molar ratio. (f) after first melting, the high temperature melting solid forms from the low melting one. (g) a solid phase transition at 382 K and the melting are not resolved. The melting enthalpy change includes both. (h) the enthalpy change includes the smectic C-nematic transition.

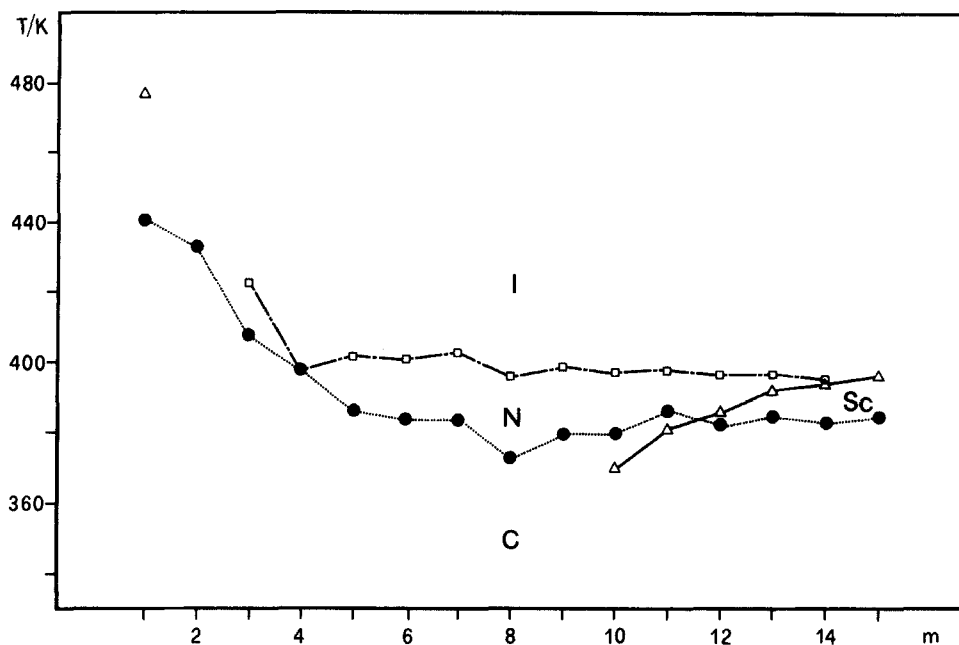


Figure 1. Phase behaviour given in a simplified form. Melting temperatures are the highest values observed for solution crystallized samples. Solid phase transitions are not reported. C (crystal phase), S_C (smectic C), N (nematic), I (isotropic). For $n = 1$ the mesophase is S_C .

evident one is the abrupt vanishing of any mesomorphic phase for the complex obtained from ethanamine ($m = 2$). This critical dependence of the mesogenic character upon seemingly minor modifications of the molecular structure is not entirely surprising, particularly when, as may happen in the present case, the structural changes affect the molecular packing along directions normal to that of major molecular elongation.

The mesogenic character shows up again with m of 3. However, the mesophase is nematic and this is the only liquid crystal phase exhibited up to $m = 9$. Smectic mesomorphism is monotropic for $m = 10, 11$, enantiotropic for $m > 11$ and it is the only one exhibited for $m = 15$. Taking 14-1NCu apart, the very general trend that favours smectic mesomorphism as the length of the flexible terminal chains increases, is parallel to that observed for the homologous set of n -1NCu compounds. A peculiar sort of odd-even fluctuation affects the thermal stability interval of the mesophase for $m = 1-5$. The odd members of the group show enantiotropic mesomorphism within temperature intervals ranging from 14.4 K ($m = 3$) to 36.5 K ($m = 1$). In contrast, no mesophasic behaviour is exhibited by 14-2NCu (the melt crystallization may take place with a supercooling of the isotropic liquid as large as 12 K) and only monotropic mesomorphism occurs for 14-4NCu. The smectic phase which is exhibited for $m > 9$ is of C type in all cases. Fan or schlieren textures were commonly observed, frequently both of them. Figures 2 and 3 are for 14-13NCu taken as an example.

X-ray diffraction spectra were recorded at 392 K for 14-14NCu and at 393 K for 14-15NCu. They are characterized by a diffuse halo around $\theta = 9.5^\circ$ and one sharp, very strong Bragg diffraction line (a very faint second order is also detectable)

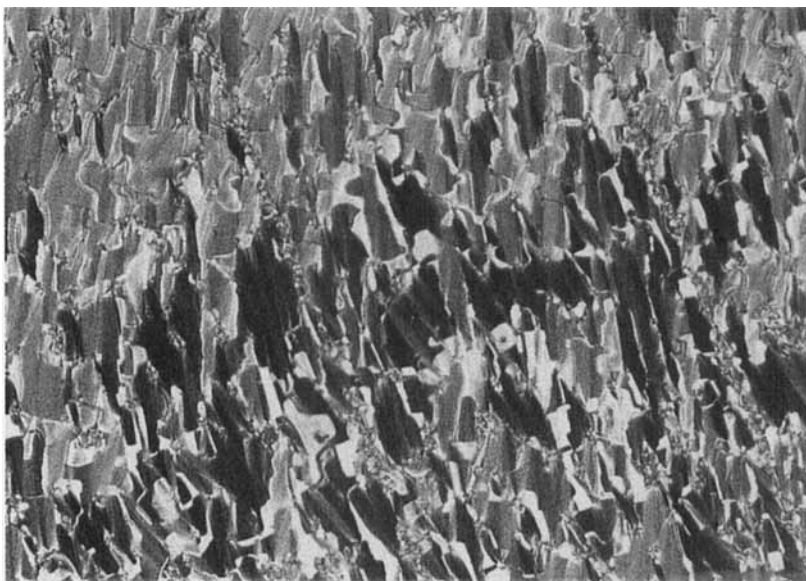


Figure 2. 14-13NCu. Smectic C phase, fan texture. $T = 390$ K. Crossed polarizers.

corresponding to a smectic layer separation of 35.3 ± 0.5 Å and 36.3 ± 0.5 Å for the two compounds respectively. These values are remarkably smaller than the smectic periodicity measured for 14-1NCu (43.3 Å, [1]) at 468 K. This feature clearly indicates that, notwithstanding the phase homology, the molecular packing within the smectic layers must have undergone a significant change. The same conclusion is suggested by the analysis of the enthalpic data. The enthalpy of transition to the isotropic phase *per unit mass* measured for 14-15NCu is considerably larger than found for 14-1NCu. On the other hand, it is apparent that the presence of the alkanamine chains has no particular influence, *per se*, on the enthalpy (*per unit mass*) of the nematic phase, in which no special restrictions are put on the molecular positions but for a partially uniform orientation. The nematic–isotropic transition enthalpies, which depend significantly on m only for $m > 8$, are even smaller than most of those measured for the n -1NCu series ($\Delta H(N - I) = 2.92$ kJ mol⁻¹ for n -1NCu, 2.88 kJ mol⁻¹ for 14- m NCu). This feature is consistent with literature data on what seems to be a general trend: organometallic nematogens exhibit comparatively low isotropization enthalpies per unit mass [2, 5].

The solid phase behaviour of most compounds of the series 14- m NCu is made complicated and not always reproducible by the occurrence of solid polymorphism according to sequences that may depend on heating or cooling rates. Inasmuch as it influences the melting behaviour and the onset of the liquid-crystalline phases we shall report it briefly. The good reproducibility of the transition temperature to the isotropic phase and the enthalpy change which has been observed through successive thermal cycles for all compounds excludes the possibility that the solid state behaviour might be influenced by any appreciable chemical decomposition taking place at the highest temperatures or by the occurrence of any dramatic form of structural isomerism (as, for example, the very unlikely *cis*-coordination of the ligands which, in any case, should occur for all compounds). In contrast, some form of conformational isomerism associated with the rotation of the *p*-alkoxybenzoate group with respect to the



Figure 3. 14-13NCu. Smectic C phase, fan and schlieren textures. $T = 390$ K. Crossed polarizers.

salicylideneaminato group cannot be ruled out, at least in principle. However, this should have a minor effect on the overall shape and elongation of the molecule (not taking into account the flexible terminal chains). For this reason and from what follows it will become apparent that a complete elucidation would require an extensive structural investigation of the crystal phases. However, this is not a central point in this paper and the following is only a schematic picture which is not intended to be exhaustive. It is based mostly on D.S.C. and polarizing microscopy data.

14-3NCu: solution crystallized samples show a solid phase transition at 379 K. No reverse transition was observed.

14-5NCu: solution crystallized and melt crystallized samples have different melting temperatures.

14-6NCu: the solution crystallized form C_1 recrystallizes, during melting, to a second solid form C_2 having a higher melting temperature. C_1 is also obtained from the melt and a phase transition to C_2 may take place to an extent depending on the temperature variation rate. At a constant temperature scanning rate the DSC behaviour at melting is fairly reproducible during successive thermal cycles.

14-7NCu: two solid forms crystallize from solution. Only one of them, that melting at the highest temperature, crystallizes from the melt. Solution crystallization of a previous melt crystallized sample reproduces the two original crystal forms according to an approximately constant molar ratio.

14-8NCu: although the melting temperature appears to be constant, a drastic decrease of the melting enthalpy has been measured for the melt crystallized sample (76.6 kJ mol^{-1} instead of $119.2 \text{ kJ mol}^{-1}$). The X-ray diffraction spectra of the two samples are different and indicative of different crystal structures. Solution crystallization of a previously melt crystallized sample reproduces the crystal form which melts with the higher enthalpy change. The remaining thermal behaviour of the sample is completely reproducible.

14-9NCu: two solid forms crystallize from solution. Only the form melting at the lowest temperature crystallizes from the melt but it may transform to the other.

14-10NCu: A single solid form C_1 crystallizes from solution. It melts into a nematic liquid at 380.4 K. A smectic C phase is formed on cooling and, successively, a second solid phase C_2 . This may transform to C_1 or melt directly to the nematic phase at 377 K on rapid heating.

14-11NCu: as for 14-10NCu but the phase transition C_2 - C_1 always takes place before melting.

14-12NCu: a solid phase transition takes place very close to melting or crystallization.

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