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Structural study of crystalline and columnar copper (II) soaps

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A homologous series of binuclear copper (II) linear chain alkanoates together with two branched chain and one aromatic substituted copper (II) alkanoates have been synthesized and studied by polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction. All of these are crystalline at room temperature, they are mesomorphic in nature above *c.* 100°C, with the exception of copper propionate which remains crystalline up to its thermal decomposition above 200°C. A systematic study has shown that the linear chain alkanoates, starting from the pentanoic derivative, produce columnar mesophases with hexagonal symmetry. Columns of polar copper carboxylate groups are surrounded by disordered aliphatic chains, and form a two dimensional hexagonal lattice. The repeat unit in a column is a binuclear dicopper tetracarboxylate complex. Two transition regimes have been detected leading from the crystal to the columnar mesophase: one dominated by the interactions between the polar heads, the other by the interactions between aliphatic chains. In the special case of the butyric derivative, the columnar mesophase obtained is rectangular in symmetry. Instead of being oriented perpendicular to the columnar axis and superposed in a four fold helicoidal fashion, the repeat units in the columns are tilted and all shifted in the same direction with respect to one another.

1. Introduction

Binuclear structures with two metal atoms bridged by four bidentate carboxylate groups are frequently observed in transition metal chemistry [1]. Copper (II) acetate hydrate was the first characterized example of such a structure [2]; subsequently, this type of complex was also found in many other copper (II) carboxylates with longer paraffinic chains [3]. We have shown recently that fatty acid complexes of copper (II), which are crystalline at room temperature, exhibit columnar liquid-crystalline phases at temperatures above *c.* 120°C [4, 5]. Still existing as binuclear units in the mesophase, the polar cores of the soap molecules are stacked to form columns indefinite in length, surrounded by the paraffinic chains with disordered conformations. Oriented parallel to each other, the columns are assembled following a two dimensional hexagonal lattice. This type of mesomorphic structure is actually identical to that exhibited by disc-like molecules such as hexasubstituted benzene [6] or triphenylene [7] derivatives, or else by molecules belonging to the class of metal complexes, more closely related to copper alkanoates, such as bis(3,4-nonyloxybenzoyl)methanato-copper (II) [8].

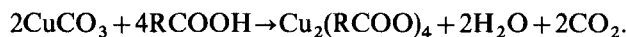
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In previous reports, we have described our investigations by X-ray diffraction of the crystalline and columnar phases of an extensive series of linear chain copper (II) alkanooates with the number of carbon atoms in the range from 12 to 22 [5]. As described later, these investigations have now been extended to further members of the series with the number of carbon atoms between 3 and 24, as well as to copper soap molecules with alkyl or phenyl substituted paraffin chains. The experimental techniques we have used to probe the structure of the mesophases are X-ray diffraction, hot stage polarizing microscopy, and differential scanning calorimetry.

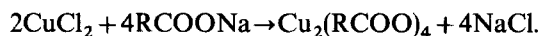
2. Materials

The general formula $(RCO_2)_4Cu_2$ defines the copper (II) alkanooates studied in the present work. In the linear chain compounds, C_nCu , R is $CH_3(CH_2)_{n-2}-$ with $n = 3, 4, 5, 6, 7, 8, 9, 11, 15$ and 24 . In the branched chain compounds, C_aCu and C_bCu , R is respectively $CH_3(CH_2)_3C^*H[CH_2CH_3]-$ and $[CH_3(CH_2)_8]_2CHCH_2-$. In the phenyl substituted compound, C_pCu , R is $CH_3(CH_2)_7OPh-$.

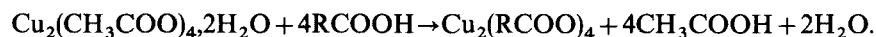
The chemical behaviour of dicopper tetracarboxylate complexes in solution was found to vary to a great extent due to the variety of aliphatic chains that have been investigated. Three different synthetic methods have been used, depending on the number of carbon atoms in the carboxylate ligand. For the shorter chains, i.e. C_3 and C_4 , an acid-base reaction between a copper carbonate salt and the carboxylic acid in aqueous solution was used [9]



For intermediate chain lengths, the copper complexes were synthesized by reaction of a copper salt (chloride of sulphate) with the sodium salt of the corresponding acid [10] in aqueous media, according to



This method was employed for linear chain compounds ($n = 5$ to 10), the branched chain complexes C_aCu and C_bCu , and for the phenyl substituted compound C_pCu . The synthesis of longer chain derivatives ($n = 11, 15$ and 24), starting with copper acetate, involves the substitution of the four acetate ligands by the corresponding fatty acid, as described in [9]:



Experimental procedures as well as characterization of all complexes are described in the Experimental.

3. Results and discussion

3.1. Optical microscopy

Optical observations proved difficult because of the thermal decomposition of the samples above $200^\circ C$, at temperatures lower than the clearing point into the isotropic liquid. As a result, the usual procedure allowing us to obtain clear and well developed characteristic textures of the mesophases, which consists of carefully cooling the sample from the isotropic liquid, could not be applied. Although the exact nature of the mesophases involved could not be safely identified optically, their occurrence from the crystal in the specific case of C_nCu could nevertheless be easily detected, and the corresponding transition temperatures were found to be consistent with those measured by differential scanning calorimetry (see table 1).

Table 1. Transition temperatures, molar enthalpies, of the linear chain copper alkanoates C_nCu with $4 < n < 12$, $n = 15$ and 24 . T_1 and T_2 were obtained by differential scanning calorimetry and polarizing microscopy respectively; enthalpies were calculated for dimers.

n	$T_1/^\circ C$	$T_2/^\circ C$	$\Delta H/kJ mol^{-1}$
5	111	—	31.5
6	95	95	29.6
7	92	93	29.2
8	85	88	35.2
9	99	102	46.0
11	107	110	64.4
15	110	108	96.1
24	120	121	194.0

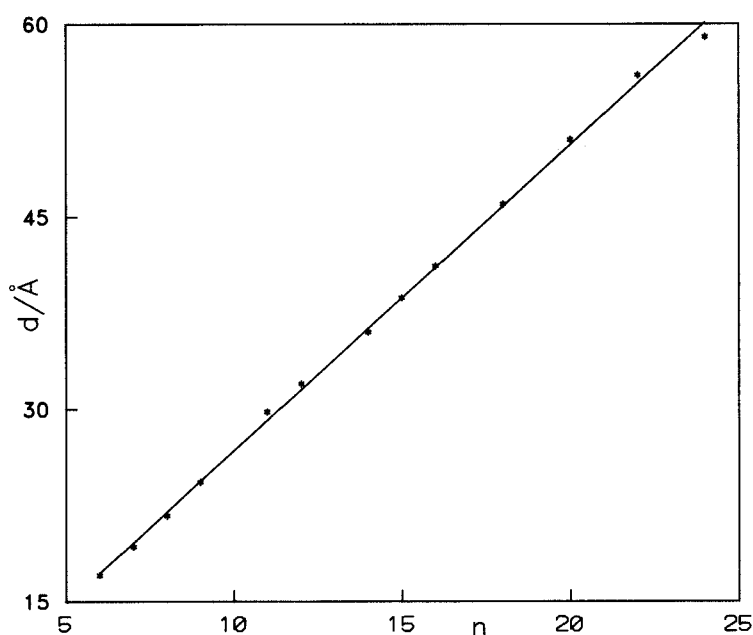


Figure 1. Lamellar spacing of the crystalline phase of linear chain copper alkanoates (C_nCu) at room temperature as a function of the number of carbon atoms in the corresponding fatty acid. Data for $n > 11$ are taken from [5].

3.2. X-ray diffraction

For the linear chain copper alkanoates (C_nCu) with $n > 5$, the X-ray patterns recorded at room temperature contain a series of sharp equidistant Bragg reflections in the low angle region, indicative of a lamellar structure, and a number of also sharp reflections in the wide angle region, consistent with a well developed three dimensional crystalline structure. These patterns are similar in every way to those published previously for the higher members of the C_nCu homologous series [5]. Independent of temperature, the lamellar spacing was found to increase linearly with n as shown in figure 1. A least-square linear fit of the measured values of b versus n gives

$$d/\text{\AA} = 2.60 + 2.41n.$$

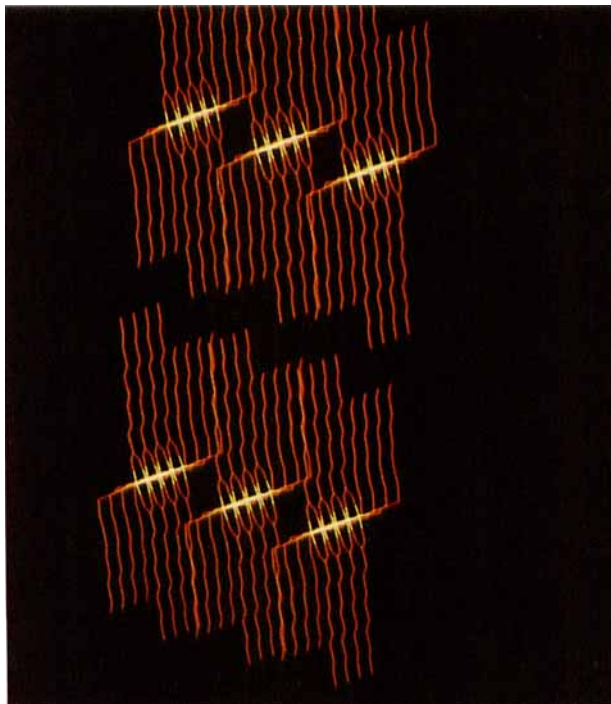


Figure 2. Lamellar molecular arrangement in the crystalline form of $C_{10}Cu$ from [3] (Sybyl software from Tripos).

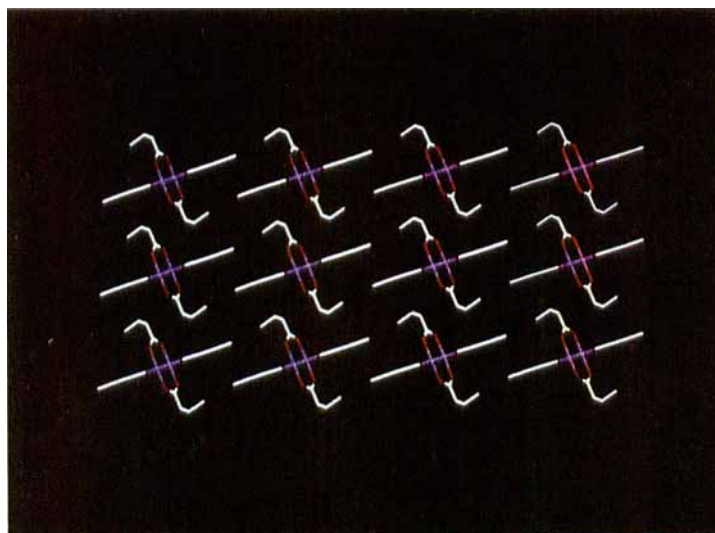
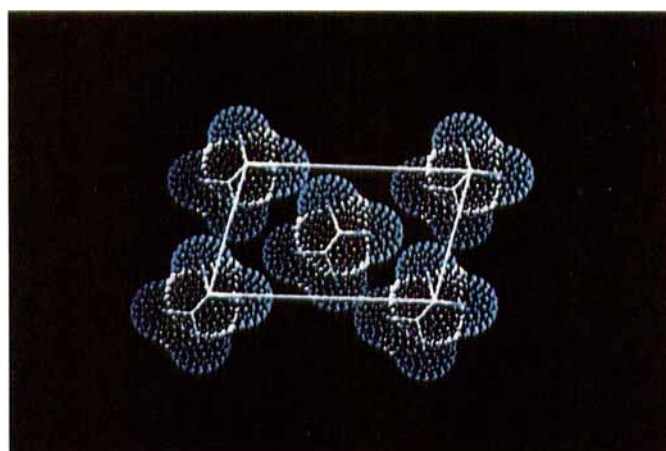
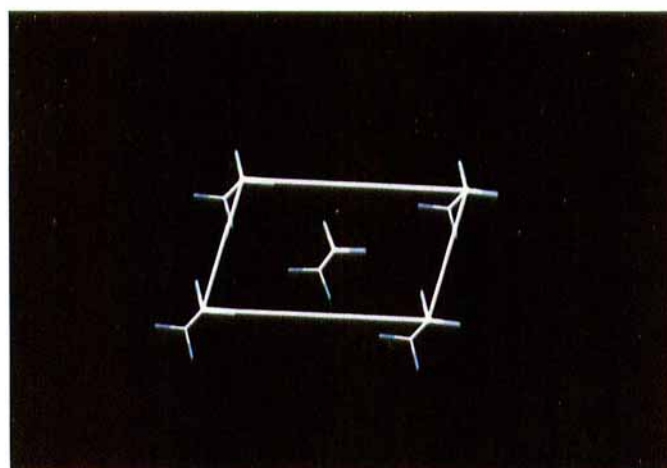


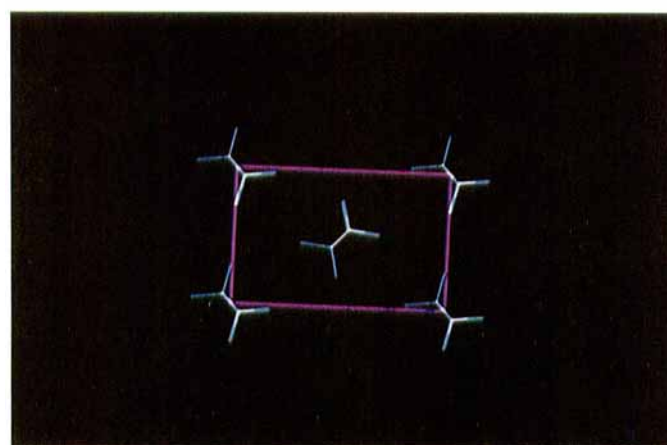
Figure 3. Molecular arrangement in the crystalline form of C_4Cu from [3] (Sybyl software from Tripos): view along the (a, b) crystallographic plane (this view corresponds in fact to the section of the columnar stacking of molecules in the crystal).



(a)



(b)



(c)

Figure 4. Lateral packing of alkyl chains (Sybyl software from Tripos): (a) Atomic filling of the subcell in a plane parallel to the lamellae and going through the aliphatic chains (see figure 2). (b) Schematic view of the bond orientation corresponding to (a). (c) Schematic view of the chevron type bond orientation in classical orthorhombic paraffin crystals.

From the slope of the corresponding straight line, and assuming a value of 2.54 Å for the length of one zig-zag of carbon atoms in a fully extended paraffin chain, we may determine the tilt angle of the alkyl chains in the C_nCu crystals to be 18° , which agrees perfectly both with the tilt angle found crystallographically with single crystals [3] and with that (18°) permitted by a triclinic closest packing of fully extended linear paraffin chains (see pages 183 and 190 in [11]).

Crystallographic studies of single crystals have been reported in the literature for the particular cases of $n=2, 3, 4$ and 10 [2, 3]. These show first of all that the copper carboxylate groups form dimers, in which four bidentate carboxylate groups bridge the two metal atoms in a lantern-shaped structure (see figure 1 in [5]). They then show that, for $n=10$, the dimeric polar cores are juxtaposed in plane layers separated from one another by double layers of extended aliphatic chains oriented at an angle with respect to the layer normals (see figure 2). They finally show that, for two of the four alkyl chains of the dimers, whatever their length, the conformation of the three methylene groups nearest to the polar core is not zig-zag planar as for the others, but twisted, presumably for steric reasons, in a nearly *gauche* conformation (see figures 2 and 3). This leads to a rotation of the zig-zag plane of the distal parts of the long alkyl chains and, as a result, to a lateral packing of the chains with all the zig-zag planes parallel to one another (see figures 4(a) and (b); such a packing is at variance with the chevron-type packing systematically obtained with paraffins in the crystalline state (see figure 4(c)) [12]. Because of the twisted conformation of half of the alkyl chains next to the polar core, the crystalline structure of C_nCu with $n=5$ is not lamellar in an evident way (only one harmonic in the low angle diffraction region of the X-ray pattern is visible), and hence we did not include it in figure 1. It is of interest to note finally that the structure of the aromatic C_pCu in the crystalline state below $70^\circ C$ was also found to be lamellar with a stacking period of 35.8 Å. In contrast, the structure of the branched chain C_aCu and C_bCu could not be described in terms of a lamellar structure; none of the basic Bragg reticular planes give rise to a sufficiently large number of harmonics in the X-ray patterns.

In the temperature range from about $100^\circ C$ up to the thermal decomposition temperature ($200^\circ C$), the X-ray patterns of C_nCu with $n > 4$ were found to be similar to the corresponding patterns of C_nCu with $11 < n < 23$ previously reported [5]; they are indicative of the same hexagonal columnar mesophase. From the low angle Bragg reflections related to the two dimensional hexagonal packing of the columns, we can very easily deduce the intercolumnar distance, D , for each member of the homologous series. The plot of D^2 as a function of n (see figure 5) turns out to be perfectly linear over the whole range from $n=5$ to $n=24$. A linear least square fit of the experimental data leads to

$$D^2/\text{\AA}^2 = 45.5 + 28.7n,$$

with a reliability factor of 99.73 per cent. The standard deviations are 9.5 for the Y intercept and 0.4 for the slope of the corresponding straight line. The stacking period h of the dimers within the columns is, therefore, totally independent of the length of the alkyl chains; assuming additivity of the partial molar volumes, and using the known value of the volume of one methylene group in a disordered state (28.8 \AA^3 at $140^\circ C$ [5]), we can deduce from the slope: $h=4.6 \text{ \AA}$, which agrees with the experimental value deduced from the X-ray pattern [5].

At $140^\circ C$, the X-ray patterns for C_bCu are similar in every way to those found for C_nCu ; evidently, the branched architecture of the alkyl chains does not perturb the

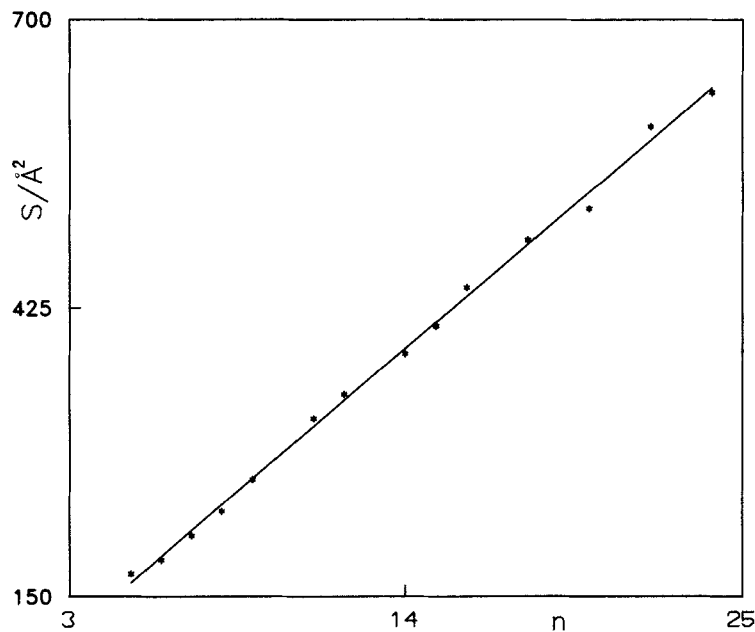


Figure 5. The area of the two dimensional hexagonal unit cell ($S = \sqrt{3} D^2/2$) as a function of the number of carbon atoms in the corresponding fatty acid.

hexagonal columnar liquid-crystalline order. This is, of course, easy to understand since all irregularities are efficiently washed out by the liquid-like conformation of the alkyl chains. This disordered conformation also explains the fact that the inter-columnar distance of C_6Cu , is 24.8 Å, in good agreement with that calculated ($D^2 = 45.5 + 28.7n$; for $n = 21$: $D = 25.5$ Å) for $C_{21}Cu$, the molecules containing the same number of carbon atoms; indeed, the alkyl chains being strongly intertangled as in a liquid and not interdigitated in the columnar structure as stated sometimes in the literature, their participation in the structure goes more through their volume than their length. From the position in the wide angle region of the X-ray patterns of a rather narrow diffuse band, separated from the diffuse band due to the liquid aliphatic chains, the stacking period of the dimers within the columns may easily be determined. The value found, $h = 4.9$ Å, is slightly larger than that of linear chain C_nCu ; it clearly suggests that the polar cores of the columns in C_6Cu are slightly stretched owing to a steric effect related to the branching at the carbon atoms closest to the polar heads.

Always at 140°C, the X-ray patterns of C_aCu and C_pCu contain the sharp Bragg reflections indicative of a hexagonal packing of elongated (columnar) diffracting elements with cell parameters of 15.0 and 23.7 Å, respectively. However they also contain quite a few additional sharp peaks, indicative of a three dimensional order; we did not try to analyse these because of their insufficient number.

The case of C_4Cu , the shortest representative of the linear chain copper alkanooates under consideration producing a columnar mesophase (C_3Cu remains crystalline up to the decomposition temperature), deserves special discussion. The melting temperature of its two three dimensional forms being high (195°C), it is extremely difficult to observe the columnar mesomorphic phase occurring at higher temperatures without severe thermal decomposition of the samples during the X-ray experiments. The diffraction

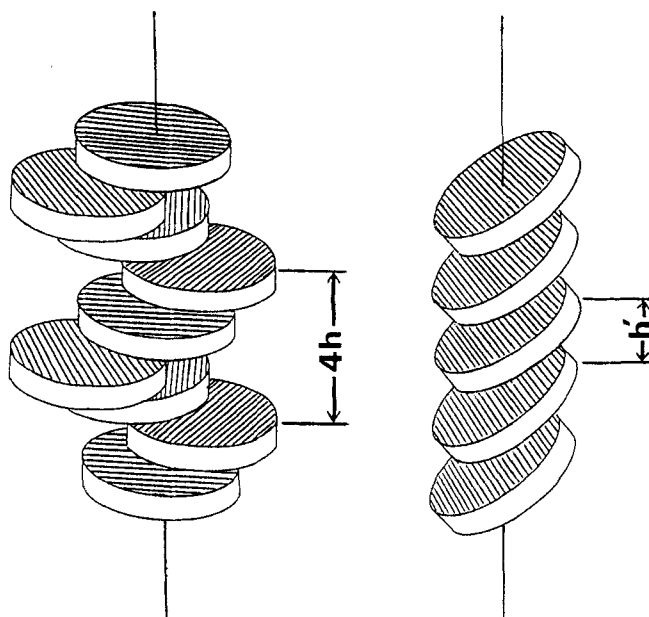


Figure 6. Schematic representation of the normal four fold helicoidal and the tilted stacking of dimers within the columns: $h = 4.6 \text{ \AA}$, measured stacking period in hexagonal columnar phase, $h' = 5.7 \text{ \AA}$, calculated stacking period in the rectangular columnar phase.

patterns at 206°C showed clearly, however, the presence of three sharp Bragg reflections all located in the low angle region, compatible with a two dimensional rectangular lattice having cell parameters $a = 11.6 \text{ \AA}$ and $b = 9.6 \text{ \AA}$, giving for each column a cross sectional area ab of 112 \AA^2 . By comparing, at constant molar volume, this area to that which we should have obtained if C_4Cu were like the higher members of the series in a columnar mesomorphic state with hexagonal symmetry (139 \AA^2 , by extrapolation from figure 5), we deduce for h a value of $(139/112)4.6 = 5.7 \text{ \AA}$. With this result, we suggest that the internal structure of the columnar cores of C_4Cu is different from that of all the higher members of linear chain copper alkanoates in the columnar mesomorphic state. To comment on this difference it is useful to recall the structure of C_4Cu in the crystal state [3]. Close inspection of the experimental data shows that, within the three dimensional structure, the dimers are in fact arranged in well-defined columns (see figure 3) with a repeat distance of 5.2 \AA . It would seem, therefore, that the columns in the rectangular mesophase are very similar to those preexisting in the low temperature three dimensional state. Their difference in regard to the columns found for the columnar mesophases of C_nCu with hexagonal symmetry is that the superposed dimers are tilted and all are shifted in the same direction with respect to one another in the case of the rectangular mesophase, whereas they are shifted in four directions and oriented normal to the columnar axis [13] in the case of the hexagonal mesophases (see figure 6). This particular behaviour of C_4Cu might be due to the short length of the alkyl chains which, located next to the polar cores, are little mobile [14] and hence unable to fill the intercolumnar space so easily as in the case for longer chains.

To conclude this section on X-ray diffraction, it is important to point out the special polymorphic behaviour of C_pCu . This aromatic substituted copper soap displays an additional mesomorphic phase above 175°C prior to thermal degradation. Stable upon cooling to 150°C , this mesophase turns out to be disordered smectic in nature, with a lamellar period of 27.3 \AA . The occurrence of such a phase might be explained by the melting of the columns and the disordering of the polar heads in a way similar to that observed for sodium soaps [15] which exhibit columnar mesophases up to 250°C with the polar heads regularly arranged within ribbon-like cores, and a smectic A mesophase at higher temperature, with the polar heads arranged in layers in a liquid-like fashion. The melting in C_pCu is no doubt due to the polarity of the aromatic rings.

3.3. Differential scanning calorimetry

The thermograms of the linear chain C_nCu alkanates are similar to those previously obtained for $11 < n < 23$ [5]; upon heating, they show an exothermic peak at a temperature between 85 and 111°C , which corresponds to the transition from the crystalline to the hexagonal columnar liquid-crystalline phase. As expected, the reverse transition upon cooling occurs at temperatures significantly lower (by about 30°C), because of the usual problems associated with nucleation and crystal growth kinetics. The whole set of transition temperatures measured, together with the corresponding enthalpies are reported in table 1. For the particular case of $n=4$, the thermograms show two peaks at 127 and 195°C , corresponding to the occurrence first of a three dimensional phase, then of the two dimensional rectangular columnar mesomorphic

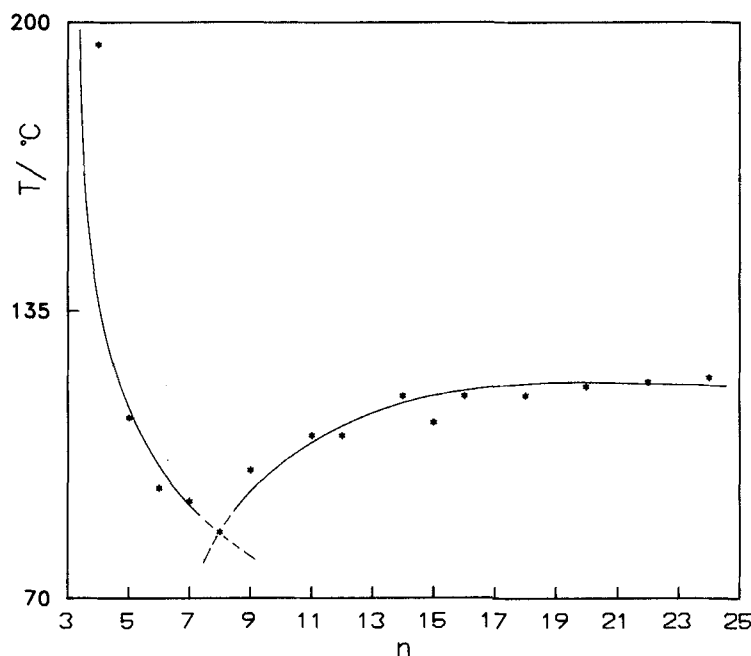


Figure 7. Crystal to mesophase transition temperatures as a function of the number of carbon atoms in the fatty acid of the copper (II) alkanates. Data from previous work on soaps with $11 < n < 23$ are also included. Full lines are only guides for the eyes.

phase, whose thermal stability is, however, extremely limited owing to the thermal degradation of the product above 200°C.

As the number of carbon atoms in the paraffin chains is increased from four, the transition temperature initially drops sharply, then grows again to level off beyond $n=14$ (cf. figure 7). This behaviour is commonly observed with alkyl side chain polymers (cf. figure 3 in [16], and figure 2 in [17]). The two regimes detected are connected with the relative parts played in the transition by the paraffin chains and the polar copper carboxylate headgroups. The decreasing regime observed with short alkyl chains corresponds to the lowering of the thermal stability of the crystals, whose structure is mainly determined by the headgroups and perturbed by the alkyl chains; the increasing regime observed with long alkyl chains corresponds to the asymptotic enhancement of the thermal stability of the crystals whose structure is dominated, instead, by the ordering of the paraffin chains.

Considering now the enthalpies involved (see figure 8), these increase linearly with the number of the methylene groups in the alkyl chains starting from $n=8$, that is the increasing melting temperature regime: $\Delta H \text{ kJ mol}^{-1} \text{ per dimer} = 10.25n - 49.51$. This corresponds to an enthalpy of 183 J g^{-1} for the fusion of the methylene groups which is lower than that (289 J g^{-1}) found for the fusion of the aliphatic chains of linear paraffins [18]. In our previous paper on the subject [5], we attributed this difference to the fact that either the alkyl chains are only partially disordered in the mesomorphic phase or substantially disordered in the crystalline state. With the additional information now at our disposal about the lateral packing of the alkyl chains (see figure 4), we think that the

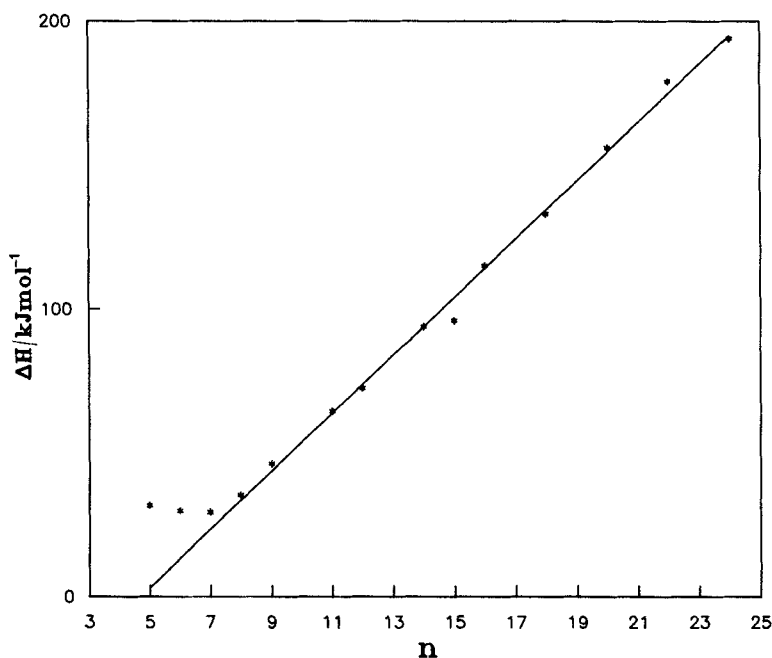


Figure 8. The crystal to mesophase transition enthalpies as a function of the number of carbon atoms in the fatty acid of the copper (II) alkanoates. Data from previous work on soaps with $11 < n < 23$ are also included.

weak melting enthalpy of the methylene groups is mainly due to the unusual arrangement of the paraffin chains. Imposed by the anchoring conditions on to the polar cores, the structure of the alkyl chains in the crystal is probably much more energetic than in ordinary paraffins. In the decreasing melting temperature regime ($n=7$), the transition enthalpies diminish with increasing n . This suggests that the shorter the alkyl chains, the larger the heat transmitted to the sample must be to overcome the strong attractive interactions of the copper carboxylate layers in the crystal, closer to one another.

The thermograms of the branched chain C_aCu and C_bCu alkanoates measured upon heating show an exothermic peak at 89 and 96°C ($\Delta H=2.9$ and 22.6 kJ mol⁻¹ respectively) corresponding to the transition from the low temperature crystal to the high temperature columnar mesophase. The thermograms of the aromatic substituted C_pCu alkanoate are more complex. They show three peaks upon heating at 74, 92 and 125°C ($\Delta H=2.9$, 46.4 and 3.3 kJ mol⁻¹ respectively). The first corresponds to a crystal-crystal polymorphic transition, and the second to the occurrence of the mesomorphic columnar phase. As for the third one, we did not try to elucidate its nature.

4. Conclusion

This investigation extends the results published previously on several long chain copper carboxylates [5]. Dealing with an extensive homologous series, we can now draw some general conclusions, based on thermodynamic and structural studies. Two important results are of special interest and their careful examination leads us to a better understanding of the mesogenic behaviour of dicopper tetracarboxylates.

We have already mentioned in this paper that the first mesogenic homologue in this series is the butyrate, C_4Cu , even if it is described here as a borderline case. It is interesting to bring together this information and the observation of the dynamic behaviour of the aliphatic chains by incoherent quasielastic scattering [14], in the mesomorphic phase. It has been shown by this technique that in the mesophase, the aliphatic chains were completely disordered except for the first four carbon atoms of each chain. This part of the carbon skeleton being closest to the metallic core is much more constrained than the rest of the chain and therefore cannot melt into liquid-like disordered state, as is the case for the carbon atoms further from the core. This means that mesomorphic behaviour can occur only if the aliphatic chains have enough available space to disorder. Our study of the case of copper carboxylates has shown that this condition is fulfilled with a chain length of at least four carbon atoms for each carboxylate.

The second result worth mentioning concerns the structure of the bimetallic core, as probed by EXAFS [13]. We had concluded, from the investigation of several homologues of the series, that the environment of the copper atoms is almost identical in both the crystalline and mesomorphic phases. In the crystal, the columns already exist as chains of dicopper complexes linked together by the axial coordination of one molecule by an oxygen atom belonging to the neighbouring complex. These chains of bimetallic cores are still present in the mesophase, and form the rigid backbone of the columns, with a superposition of binuclear complexes in a four fold helicoidal fashion.

We now have a clear picture of the mesophase: an assembly of columns all parallel, made up of a rigid metallic backbone surrounded by a lipophilic fluid. The most natural organisation of such elements, in a plane perpendicular to their axis, is a compact array, and it has an hexagonal symmetry. We can conclude therefore, that the mesomorphic

properties are governed by the capability of the aliphatic chains to melt, without destroying the intermolecular cohesion of the metallic core. This conclusion is further supported by the fact that the same mesogenic behaviour has been observed for several binuclear carboxylates of metals such as Rh(II) [19], Ru(II) [20] and Mo(II) [21].

5. Experimental

5.1. Materials

All of the reagents were of commercial grade purity, except nonyl-3-dodecanoic acid which was synthesized following a procedure already described in detail elsewhere [22]. The copper complexes have all been characterized by elemental analysis (C, H, Cu) and the results are reported in table 2.

5.2. C_nCu , $n=3$ and 4

A hot suspension of 1 g of copper carbonate ($CuCO_3$) in 50 cm^3 of a water-acid solution (propionic or butyric, 1/1 volume) was stirred at 70°C for one hour: the suspension slowly dissolved and an evolution of carbonic gas was observed, as the solution was concentrated to 10 cm^3 by evaporation under vacuum on a water bath. After cooling to room temperature, the blue-green powder which formed was filtered under vacuum, then recrystallized in 30 cm^3 of a *n*-heptane/acid mixture (10 per cent acid in volume). The resulting microcrystalline powder was filtered then dried at 60°C under vacuum for 24 h. Yield: 55 per cent.

5.3. C_nCu , $n=5, 6, 7, 8, 9$ and 10; $CaCu$, $CbCu$ and $CpCu$

A solution of the sodium salt of the fatty acid was prepared by careful addition of aqueous sodium hydroxide (0.4 g NaOH, 10 mmoles, dissolved in 10 cm^3 of water) to a vigorously stirred emulsion made by 5 mmoles of fatty acid in 20 cm^3 of water. The emulsion disappeared and after stirring for an additional 15 min, the pH was brought back to 7 by addition of a few drops of concentrated sulphuric acid. A solution of 0.65 g

Table 2. Elemental analysis (C, H, Cu) of the copper carboxylates.

Compound	C		H		Cu	
	% exp.	% calc.	% exp.	% calc.	% exp.	% calc.
C_3Cu	34.36	34.37	4.76	4.81	29.41	30.30
C_4Cu	40.40	40.40	5.90	5.80	25.80	26.70
C_5Cu	45.48	45.19	6.88	6.83	23.30	23.91
C_6Cu	48.97	49.05	7.69	7.55	22.24	21.62
C_7Cu	51.96	52.24	8.21	8.14	19.53	19.74
C_8Cu	54.42	54.91	8.71	8.64	18.42	18.16
C_9Cu	56.88	57.19	9.21	9.07	15.66	16.81
$C_{10}Cu$	59.17	59.16	9.46	9.43	14.96	15.65
$C_{11}Cu$	59.85	60.87	9.74	9.75	15.48	14.64
$C_{15}Cu$	65.71	65.95	10.99	10.70	11.54	11.63
$C_{24}Cu$	71.88	72.17	11.89	11.88	8.17	7.95
C_aCu	54.33	54.92	8.70	8.64	17.87	18.16
C_bCu	70.68	70.59	12.00	11.56	8.92	8.89
C_pCu	63.90	64.17	7.80	7.61	11.27	11.29

of copper sulphate (2.6 mmoles) in 10 cm³ of water was then added slowly to the aqueous solution of sodium soap, and a blue precipitate formed. After complete addition, the resulting mixture was stirred for half an hour, then filtered under vacuum to yield a pale blue powder. The complex was purified by recrystallization in 30 cm³ of hot *n*-heptane, then filtered and dried at 60°C under vacuum for 24 h. Yield: 75 to 88 per cent.

5.4. C_nCu , $n = 11, 15$ and 24

An ethanolic solution of copper acetate (0.5 g of hydrated copper acetate in 50 cm³ of ethanol) was added slowly to a solution of 5 mmoles of fatty acid in 50 cm³ of ethanol. A pale blue powder precipitated readily, and was isolated by suction filtration. This product was purified by recrystallization in 50 cm³ of hot *n*-heptane, then filtered under vacuum and dried at 60°C under vacuum for 24 h. Yield: 80 to 90 per cent.

5.5. Optical microscopy

Transmission optical observations of thin films of material were made using a Leitz polarizing microscope fitted with a Mettler FP 82 hot stage.

5.6. X-ray diffraction

X-ray diffraction patterns of powder samples in Lindemann capillaries were recorded photographically using monochromatic Cu-K_{α1} radiation and a Guinier focusing camera equipped with a bent quartz monochromator. The equipment for variable temperature experiments has already been described in detail elsewhere [23].

5.7. Differential scanning calorimetry

Differential scanning calorimetry measurements were performed using a Perkin-Elmer DSC-2C instrument. Contained in aluminium pans, the samples were heated or cooled in a temperature range from 300 to 480 K at a scanning rate of 10 K min⁻¹.

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