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Investigation of the structures of the crystalline and columnar phases of linear chain copper(II) alkanoates

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Binuclear copper(II) complexes of fatty acids crystallize at room temperature in a lamellar lattice that has been characterized by X-ray diffraction. A transition to a thermotropic columnar mesophase is observed at about 110–120°C for each compound of the series $n = 12$ to $n = 22$, n being even and equal to the number of carbon atoms in the corresponding fatty acid. This columnar mesophase has been investigated by polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction. Columns of polar copper carboxylate groups are surrounded by disordered aliphatic chains, and form a two-dimensional hexagonal lattice. The repeating unit in a column is a binuclear dicopper tetracarboxylate complex.

1. Introduction

We have reported some preliminary results of a structural investigation by X-ray diffraction of copper(II) dodecanoate (copper(II) laurate) as a function of temperature [1]. This complex was shown to exhibit, above 107°C, a columnar mesophase which is analogous to those characterized earlier for several other soaps of group II metals [2]: the polar groups of the molecules lie on linear arrays, or columns, of indefinite length, surrounded by disordered aliphatic chains; each column lies at a node of a two-dimensional hexagonal lattice. The intercolumnar distance was found to be *c*. 20 Å for this complex [1].

Further insight into the structure of this columnar mesophase was obtained by considering the molecular structure of the core of the copper soaps. Carboxylate complexes of copper(II) are known to exist as binuclear molecules, the structure of which has been characterized by X-ray diffraction in the solid state [3]; this coordination geometry is illustrated schematically in figure 1. An approximate determination of the linear density of copper atoms along a column in the mesophase (two atoms every 4·7 Å) allowed us to reach the safe conclusion that the repeating unit within a column of copper laurate is a binuclear complex [1]. Moreover, magnetic susceptibility data obtained for several copper(II) alkanoates over a temperature range that includes the solid–columnar phase transition [4] showed that a Bleaney–Bowers relationship is obeyed in both phases, supporting the view that the columnar mesophase is made of antiferromagnetically coupled binuclear copper(II) units with little interdimer interactions.

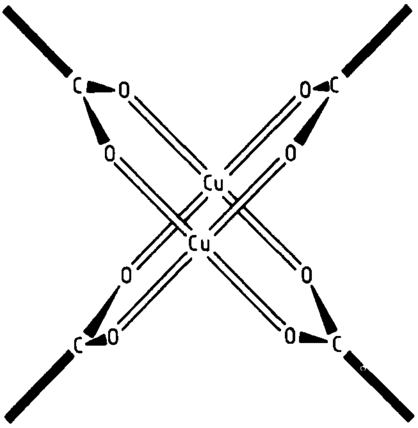

Figure 1. Schematic view of the core of a binuclear dicopper tetracarboxylate complex.

As part of a continuing investigation of the physicochemical properties of mesogenic transition metal complexes [5], we now report the complete structural details for the columnar mesophase found throughout the homologous series of complexes with general formula $Cu_2(O_2CR)_4$; $R = CH_3\text{–}(CH_2)_{n-2}\text{–}$ where n is an even number between 12 and 22. The experimental techniques we have used to probe the structure of this mesophase are differential scanning calorimetry (D.S.C.), hot-stage polarizing microscopy and X-ray diffraction.

2. Experimental

Copper(II) alkanoates were synthesized by reaction of the sodium salt of the appropriate fatty acid with a solution of copper sulphate or acetate in ethanol and ethanol–water respectively, depending on the length of the aliphatic chain. They were purified by recrystallization from heptane. Satisfactory elemental analyses were obtained for carbon, hydrogen and copper.

Optical observations were made with a microscope fitted with a Mettler FP 52 hot-stage. X-ray diffraction patterns of powder samples in Lindemann capillaries were recorded photographically using monochromatic copper $K_{\alpha 1}$ radiation and a Guinier focusing camera equipped with a bent quartz monochromator. The equipment for variable temperature X-ray diffraction has been described in detail elsewhere [6]. Differential scanning calorimetry was performed using a Perkin-Elmer DSC-2C calorimeter. Thermograms of samples in sealed aluminium pans were recorded over the temperature range 300–520 K at a scanning rate of $5\,K\,min^{-1}$.

3. Results

3.1. *Differential scanning calorimetry*

The thermograms that have been recorded for the entire series of linear copper(II) alkanoates ($n = 12$ to $n = 22$) all show a transition at a temperature between 110°C and 120°C. As we show later, this peak corresponds to a transition from the crystalline to a mesormorphic state. The reverse transition (mesophase to crystal) occurs at a somewhat lower temperature, because of slow nucleation and crystal growth kinetics. When $n = 12$, 18 and 22, the thermograms recorded upon heating exhibit an oscillation prior to the main peak (cf. figure 2). These pre-peaks, the shape of which depends on

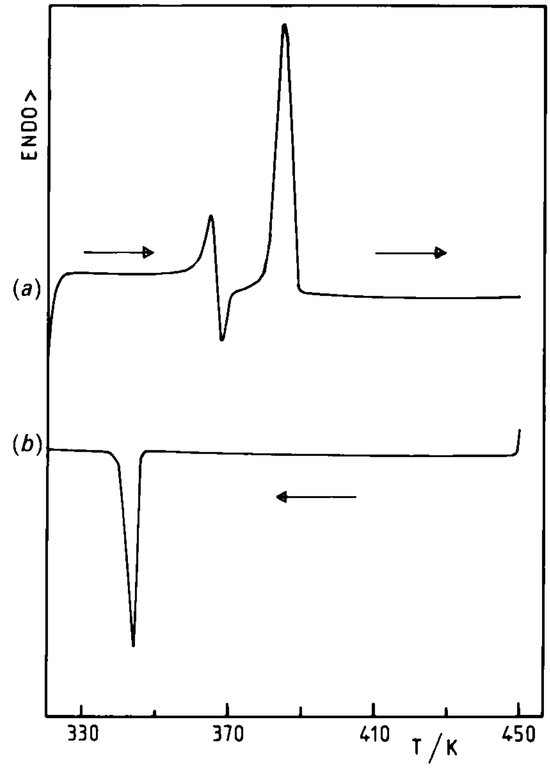

Figure 2. Heating (*a*) and cooling (*b*) D.S.C. thermograms of copper dodecanoate (n = 12). Reheating the sample gives rise to the same oscillations.

the thermal history of the sample, have not been investigated in detail. Transitions to the isotropic liquid occur above 200°C, a temperature at which thermal decomposition of the sample begins, and so they are difficult to detect.

Values of the transition temperatures and enthalpies are listed in table 1. Although the transition temperatures seem to have only a weak dependence on the length of the aliphatic chain, it appears that molar enthalpies show a linear dependence on the number, n, of carbon atoms of the chain (cf. figure 3). The corresponding slope gives an approximate value of the transition enthalpy for a single methylene group; this

Table 1. Values of transition temperatures and enthalpies for a monomeric soap molecule determined by optical microscopy (T_1) and differential scanning calorimetry (T_2 and ΔH, T_2 corresponding to the onset of the phase transition upon heating) for the crystal–mesophase transition of copper(II) alkanoates as a function of the number (n) of carbon atoms of the corresponding fatty acid.

n	T_1/°C	T_2/°C	ΔH/kJ mol^{-1}
12	110	107	35·6
14	119	116	46·6
16	117	116	57·0
18	116	116	65·7
20	121	118	79·6
22	121	119	91·7

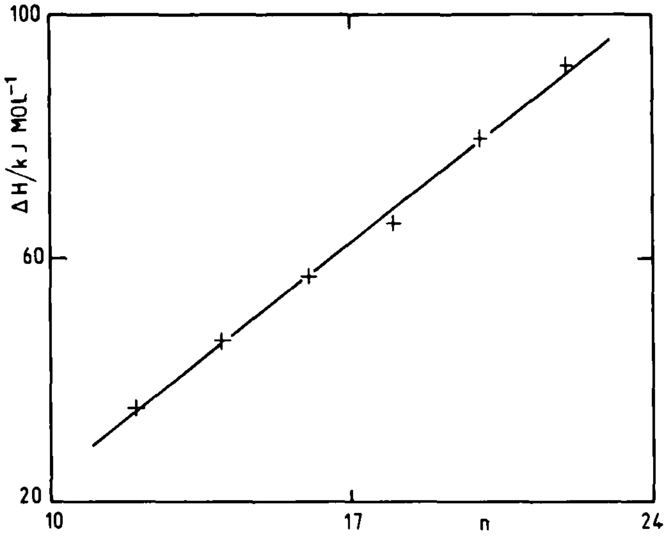

Figure 3. Molar enthalpies as a function of the number of carbon atoms of the corresponding fatty acid for the crystal to mesophase transition of copper alkanoates.

value (196 J g^{-1}) is lower than that found for the fusion of aliphatic chains of smectic mesogens (272 J g^{-1}) [7] or of linear paraffins (289 J g^{-1}) [8]. The observed difference is probably related to the fact that either the aliphatic chains are only partially disordered in the mesomorphic phase of the copper soaps, or different types of disorder are found in the crystalline phases of the three types of compounds, or both. The non-zero intercept found in figure 3 probably reflects a change in the interactions between the polar cores of the copper complexes at the crystal–mesophase transition.

3.2. *Optical microscopy*

Observations using an optical polarizing microscope were difficult due to the thermal decomposition of the samples at temperatures below the transition to the isotropic liquid. Thus, the procedure which usually gives the characteristic textures (i.e. cooling the isotropic liquid) is inadequate (see for example figure 1 in [9]). Nevertheless, we have been able to observe textures with developable units for the higher members of the series of copper soaps (cf. figure 4), indicating that the high-temperature phases have a columnar structure. As we show later, this structural assignment is fully confirmed by the X-ray diffraction data. Approximate values of the transition temperatures have been obtained by microscopic observation; they are in reasonable agreement with the values obtained by D.S.C. (cf. table 1).

3.3. *X-ray diffraction (crystalline phase)*

Diffraction patterns recorded below the transition temperatures (*c*. 100°C) exhibit, in the low Bragg angle region, a series of sharp reflections with reciprocal spacings in the ratios 1 : 2 : 3 : 4, indicating a lamellar structure. In the wide-angle region, another series of sharp reflections is observed, corresponding to periods of *c*. 3–5 Å, indicative of a well-developed short range organization. This type of pattern is entirely similar to those obtained [10] for some alkaline earth soaps at temperatures below 120°C.

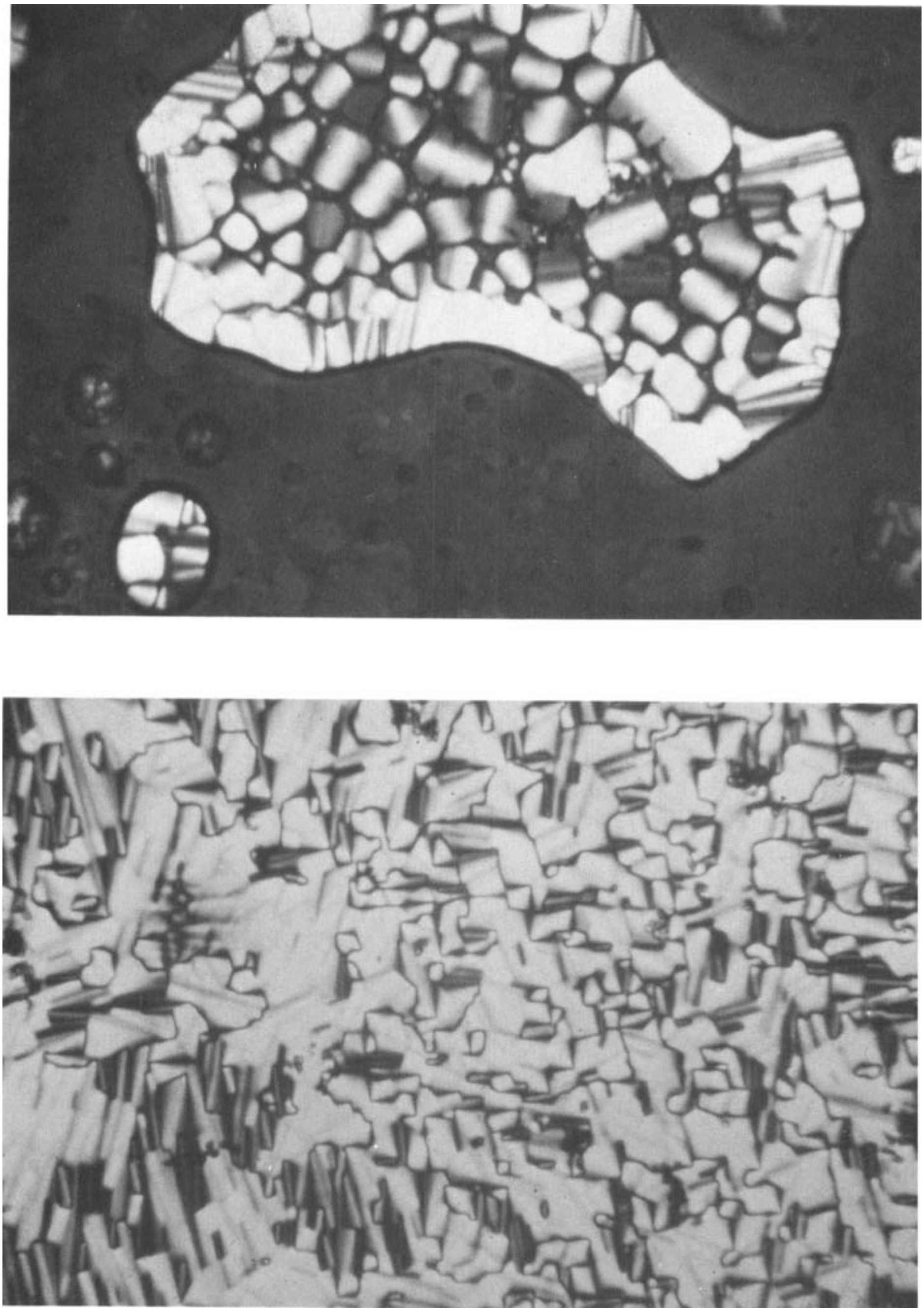

Figure 4. Optical textures observed with a polarizing microscope (×300) at 120°C for the columnar mesophase of copper docosanoate ($n = 22$).

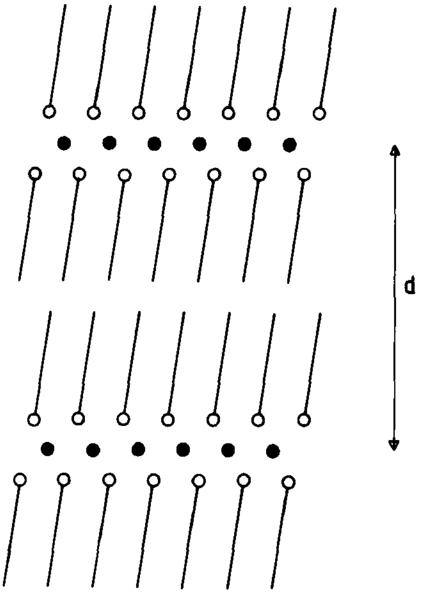

Figure 5. Schematic view of the lamellar structure of the crystalline phase of copper soaps.

The lamellar structure of copper(II) soaps in the solid state is analogous to that determined by Lomer and Perera [11] from a single crystal X-ray diffraction study of copper(II) octanoate and copper(II) decanoate. The polar cores of the molecules lie on parallel planes separated by two layers of paraffinic chains (cf. figure 5). The interplanar distance, d, is independent of temperature for a given compound of the series (cf. figure 6), but it increases linearly with the number of carbon atoms in the aliphatic chain (cf. figure 7). A least-square fit of this plot gives the equation

$$d/\text{Å} = 2{\cdot}37n + 3{\cdot}6,$$

which gives a value of 2·37 ± 0·06 Å for the increase in interplanar distance due to two carbon atoms. Comparison with the value of 2·54 Å found for a normal paraffin in the crystalline state indicates that in the copper soaps the average direction of the chains lies at an angle of *c.* 20° with respect to the perpendicular to the layers. On the other hand, the value of 3·6 ± 1 Å found for the intercept compares reasonably well with that of 4–5 Å determined [10] for other group II metal soaps.

Finally, the molecular area, S, occupied by an aliphatic chain in a layer plane can be obtained from the relationship

$$S = V/N_A d,$$

where V is the molar volume, d the interplanar distance, and N_A the Avogadro constant. A value $S = 20{\cdot}8\,\text{Å}^2$ is found for copper docosanoate ($n = 22$) for which a determination of V is available [12]. This corresponds to an actual bulkiness of the aliphatic chain 20·8 cos (20) = 19·4 Å^2, in fair agreement with the value (19–20 Å^2) usually accepted.

3.4. *X-ray diffraction (columnar phase)*

Diffraction patterns recorded above the transition temperatures exhibit in the low-angle region a series of three or four sharp reflections with reciprocal spacings in

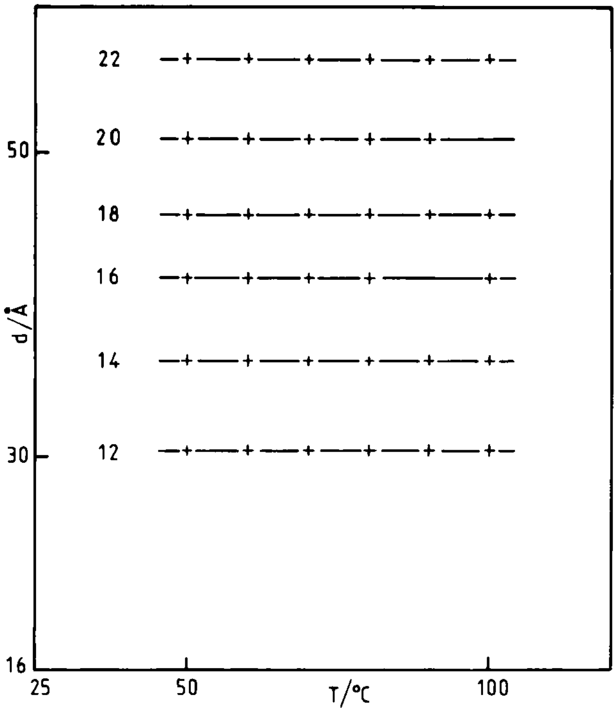

Figure 6. Lamellar spacing as a function of temperature for the crystalline phase of copper alkanoates.

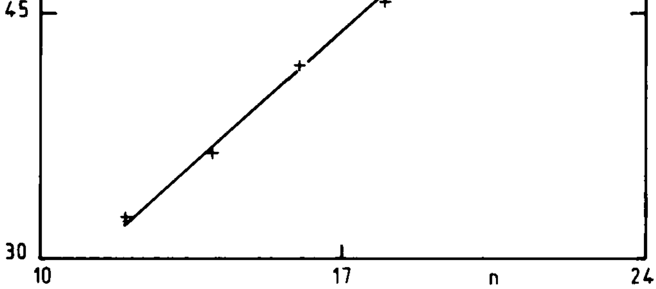

Figure 7. Lamellar spacing of the crystalline phase of copper alkanoates at 50°C as a function of the number of carbon atoms in the corresponding fatty acid.

the ratios $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, characteristic of a two-dimensional hexagonal lattice. At larger angles, a diffuse band is observed, which corresponds to a Bragg spacing of *c*. 4·6 Å. Such patterns are entirely similar to those obtained for classical columnar mesophases [13]. Thus, it can be concluded that the high temperature phase of copper(II) soaps is made up of columns in which the polar cores of the complexes are surrounded by disordered aliphatic chains; each column lies at a node of a two-dimensional lattice. The disordering of the aliphatic chains is clearly supported by a study of copper(II) octadecanoate by proton N.M.R., indicating free rotation of the hydrocarbon moieties [14].

It is possible to estimate the intercolumnar distance, D, from the values of the Bragg spacings in the low-angle region. Table 2 lists values of D at various temperatures for each compound studied in the series of copper(II) soaps. A modest increase of the intercolumnar distance with increasing temperature is observed in the temperature range 120°C to 150°C: $(1/D)\ (dD/dT) = 4 \times 10^{-4}\,\mathrm{K}^{-1}$. Above 150°C, the thermal expansion of the columns is apparently much larger, but this probably reflects the thermal decomposition of the sample. Degradation products would dissolve in the aliphatic domains, leading to a large increase in the intercolumnar distance; such behaviour has been observed in some hydrocarbon–soap mixtures [15].

Table 2. Values of the intercolumnar distance D at 140°C for the columnar mesophase of copper(II) alkanoates as a function of the number, n, of carbon atoms of the corresponding fatty acid.

n	D/Å
12	19·9
14	21·0
16	22·6
18	23·8
20	24·5
22	26·3

As shown in table 2, the intercolumnar distance, D, increases steadily when the number of carbon atoms in the aliphatic chain of the complex increases. A plot of D as a function of n shows an apparently linear relationship, similar to that advocated earlier for other homologous series of columnar mesophases [13]. We wish to point out, however, that such an empirical correlation has no physical basis, and that the variation of D^2 as a function of n should be plotted instead. As a matter of fact, D is comparable to the length of a molecule of fatty acid in its all-trans configuration, whereas the aliphatic chains are disordered in the columnar phase, Moreover, the two-dimensional character of the array of columns precludes a linear dependence of D on n, as explained later.

It is useful to recall a more rigorous analysis of this problem which was proposed some time ago for the columnar mesophases of alkaline earth metal soaps [15], and which has been used successfully again for the columnar mesophases of truxene derivatives [16]. A simple calculation shows that the overall volume, V, of a binuclear complex in a column is given by

$$V = (\sqrt{3}/2)hD^2 = V_a + 4nV_p,$$

where h is the average distance between binuclear units along the column axis, V_a is the volume of the polar core and V_p is the volume of a methylene group. It has been shown for alkaline earth metal soaps that h and V_p are independent of n, and it is reasonable to assume that this is true also for copper(II) soaps. Thus, a plot of D^2 versus n should be linear according to this simple model. As shown in figure 8, this

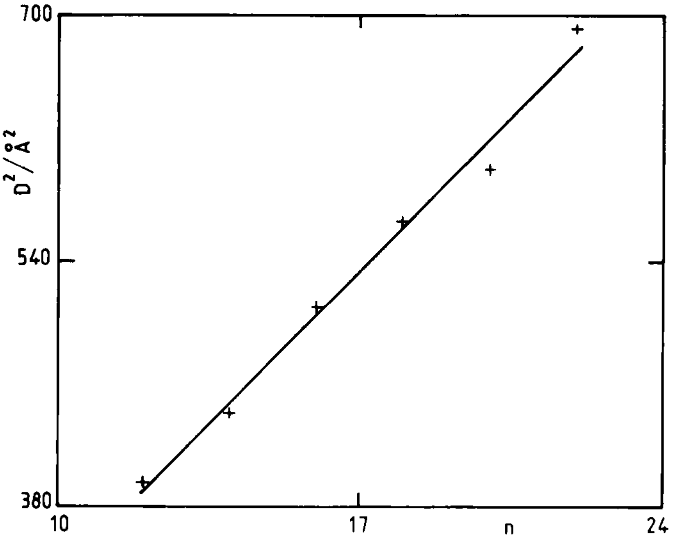

Figure 8. Square of the intercolumnar distance as a function of the number of carbon atoms of the corresponding fatty acid for the columnar mesophase of copper alkanoates at 140°C.

is in fact what we observe in the present study; a least-square fit of the data gives the linear relationship

$$D^2/\mathrm{Å}^2 = 45{\cdot}8 + 28{\cdot}7n$$

at 140°C. Several investigations have shown that, at a given temperature, V_p has a constant value, independent of the type of mesophase and of the chain length, i.e. about 28·8 $\mathrm{Å}^3$ at 140°C [17]. This observation is reasonable since the aliphatic chains are generally disordered. It is therefore possible to estimate h, the average distance between binuclear units in a column, from the slope of the D^2 versus n plot

$$8V_p/h\sqrt{3} = 28{\cdot}7.$$

This distance ($h = 4{\cdot}64 \pm 0{\cdot}06$ Å) is in fair agreement with that determined earlier [1] for copper(II) dodecanoate using an experimental determination of D and an estimate of the molar volume V (taken to equal that of other group II metal soaps).

A direct calculation of h is possible for copper(II) docosanoate ($n = 22$), for which an experimental determination of the molar volume is available, $V = 2 \times 828\,\mathrm{cm^3\,mol^{-1}}$ [12]. Thus, $h = 2V/\sqrt{3}D^2 = 4{\cdot}68$ Å at 140°C, in agreement with the values which we have cited. This agreement confirms the validity of the assumption that h and V_p are independent of n, as well as that of the structural model in which the repeating unit in a column is a binuclear complex with its copper–copper axis along the column spine, corresponding to a period of about 4·6–4·7 Å.

Further insight into the stacking of the binuclear complexes could be gained by the examination of the wide-angle reflection at 4·6–4·7 Å. Unfortunately, the diffuse band around this Bragg spacing reflects also the disorder of the aliphatic chains, which cannot be resolved from the stacking period of the polar cores.

A final comment can be added concerning the value found by extrapolation to $n = 1$ of the D^2 versus n plot, corresponding to a hypothetical column of binuclear copper formate units. The radius of such a column can be calculated from this value, and it is found equal to *c*. 4·5 Å, consistent with crystallographic data on copper(II) carboxylates [18].

4. Conclusion

The present investigation has shown that, contrary to the conclusion of an earlier study [19] which suggested that the $n = 12$, 14 and 16 copper(II) alkanoates melt directly from crystal to isotropic liquid, while the $n = 10$ and 18 derivatives actually give rise to a mesophase upon heating, all members of the homologous series of linear chain copper(II) alkanoates in the range from $n = 12$ to 22 show a thermal behaviour identical to that of copper(II) dodecanoate [1]. At room temperature, their crystalline structure is of a lamellar type, in which planes of polar copper carboxylate groups are separated by a double layer of aliphatic chains, the latter being slightly tilted with respect to the perpendicular to these planes. At higher temperatures (> 120°C), they exhibit a columnar mesomorphic structure, in which columns of polar groups are surrounded by disordered aliphatic chains and form a two-dimensional hexagonal lattice. The repeating unit in a column is a binuclear dicopper tetracarboxylate complex, with a stacking period independent of the number of carbon atoms of the chain. It is interesting to note that a thermotropic mesophase had been reported earlier for copper stearate, but that its columnar structure had not been recognized [9, 14].

A more detailed analysis of the columnar structure of copper(II) alkanoates will have to await the results of a copper K-edge EXAFS study now in progress. It is hoped that a comparison of the bond lengths in the coordination sphere of copper above and below the phase transition will be possible by this technique; this would afford a better understanding of the solid–discotic transition at a molecular level. Further developments are also expected from dilatometric experiments, presently being completed, and from the investigation of the effects of various substituents in the chains on the structure of the mesophases.

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