Pergamon

*Spectrochimica Acta*, Vol. 51A, No. 3, pp. 341–347, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0584–8539(94)00128–6
0584–8539/95 $9.50 + 0.00

# Spectroscopic study of the phase transitions of copper(II) n-alkanoates

M. I. REDONDO,† M. V. GARCÍA, M. J. GONZÁLEZ-TEJERA and J. A. R. CHEDA
Departamento Química Física I, Facultad de CC, Químicas, Universidad Complutense, 28040 Madrid, Spain

(*Received* 14 *March* 1994; *in final form* 8 *May* 1994; *accepted* 9 *May* 1994)

**Abstract**—FTIR spectra of copper nonanoate, decanoate, undecanoate and dodecanoate are recorded every 5 K from room temperature to 390 K. Changes detected in the infrared spectra when heating the sample allow the heat absorptions observed in some of these samples prior to the transition to the mesophase to be explained as due to conformational changes taking place in the alkyl chain next to the carboxylate group. Low frequency infrared and Raman spectra are consistent with a $D_{4h}$ geometry for the ionic core where the copper ions are located. Moreover, the study of the low frequency region at the temperature of the mesophase permit the detection of rearrangements around the central core in the transition from the crystal to the mesophase.

## INTRODUCTION

The organic salts of metallic ions have considerable importance both from an industrial and structural point of view [1], mainly due to their thermo and lyotropic mesomorphism (plastic and ionic crystals). Because of this much scientific work has been devoted to this kind of compounds. Tl(I), K, and Pb(II) n-alkanoates have been studied in our laboratories in order to establish their thermophysical properties [2, 3] and how these properties are related to their internal structure. Studies of DSC and temperature dependence of the vibrational spectra of these soaps have been carried out [4]. Copper(II) organic salts have received much attention in the literature [5–7] due to their characteristic discotic mesophase and their potential as one-dimensional conductors or molecular ferromagnets. So, in ref. [5] and preceding papers by the same authors a comprehensive study about the structure of linear and branched copper(II) soaps in the crystal and in the mesophase can be found. However, some facts on the thermograms of linear copper(II) soaps obtained by DSC still remain unexplained. For instance, the heat absorption and the endo–exo effects observed [6, 7] in some samples before the crystal–mesophase transition.

A simple model for thermotropic discotic phase formation involves the melting of the side chains and a rearrangement of the cores into columns at the crystal–mesophase transition. Both processes imply structural changes which can be identified by vibrational spectroscopy. In this work we accomplish a systematic study of the structural changes taking place in copper(II) nonanoate, decanoate, undecanoate and dodecanoate when heating. To do this the infrared spectra from room temperature to the mesophase were recorded every 5 K. Modifications in shape and frequency of some bands of the infrared spectra allow the heat absorptions observed by calorimetry to be explained. Raman spectra at room temperature as well as a far infrared study at different temperatures of these soaps give information about the structure of the metallic central core in the crystalline phase and in the mesophase.

## EXPERIMENTAL

Copper(II) n-alkanoates were prepared by metathesis in alkaline alcoholic solution from the corresponding fatty acid at 70°C. A stoichiometric amount of a copper sulfate saturated solution was added slowly to the ethanolic solution of the potassium carboxylates. Several recrystallizations from n-heptane and/or benzene were carried out. A Mettler FP-84 DTA connected to a FP-80 central processor was used in the thermal behaviour study.

---

† Author to whom correspondence should be addressed.

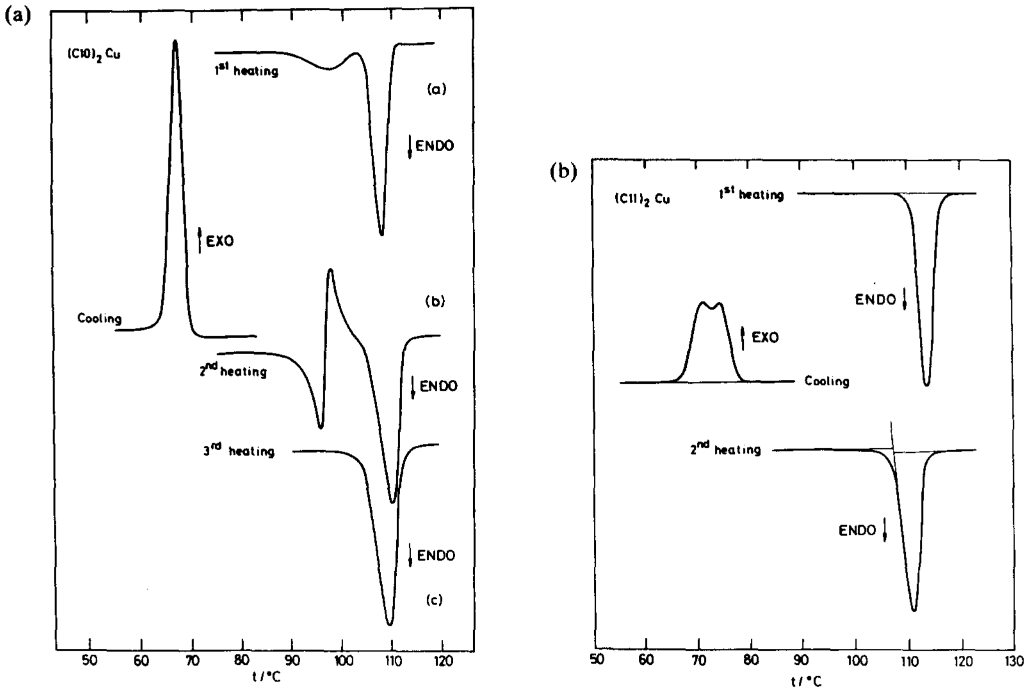

Fig. 1. Thermal behaviour of copper(II) decanoate (a) and undeconaoate (b)

Infrared spectra of Cu(II) alkanoates in KBr pellets (polyethylene pellets for far infrared) were registered using a FTIR Nicolet 60SX, at a resolution of 2 $cm^{-1}$ in the mid infrared and 4 $cm^{-1}$ in the far infrared region. A Dilor XY Raman spectrometer with a multichannel detector was used to take the Raman spectra of the compounds. An $Ar^+$ laser at 514.5 nm was the radiation source. All Raman spectra were recorded from the samples under microscope. However the intensity of the Raman signal was low and it was impossible to obtain Raman spectra at high temperature because the samples deteriorate when high laser power was used.

## RESULTS AND DISCUSSION

The copper(II) carboxylates, $Cu(Cn)_2$ with $n = 9$–$12$, were studied by DTA over the temperature range from 323 K up to their decomposition temperatures.

All samples received the same treatment: first heating from a crystalline sample freshly prepared, then cooling and reheating a second and a third time.

As an example of the thermal behaviour Fig. 1 shows the DTA curves obtained for $Cu(C10)_2$ and $Cu(C11)_2$ in the first, second and third heatings and in the cooling. As can be seen there are noticeable differences between the thermograms of both samples: in $Cu(C11)_2$ no differences between first and subsequent heatings are observed and only

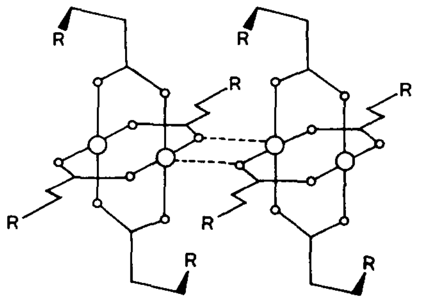

Fig. 2. Schematic illustration of the arrangement of the dimers in the crystal according to X-ray results [8–10]. O, Cu(II) ions; o, oxygen atoms.

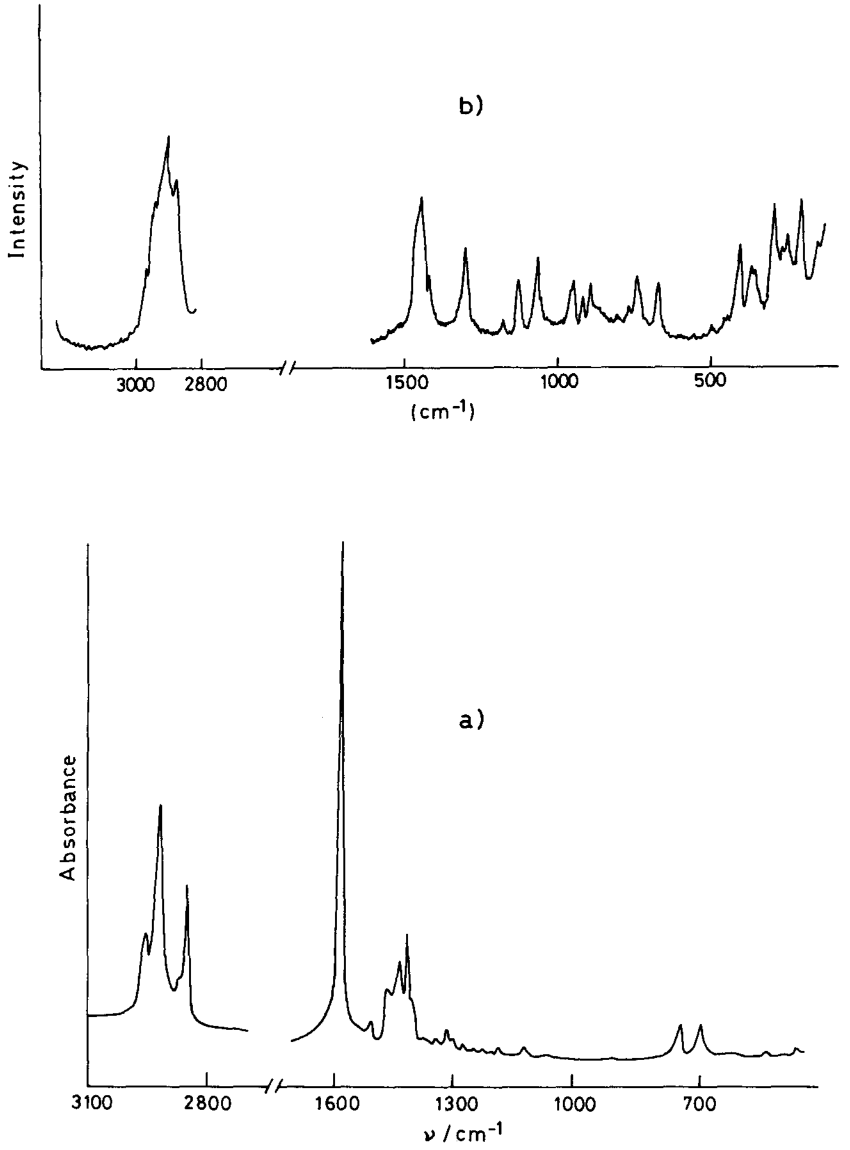

Fig. 3. Infrared (a) and Raman (b) spectra of $Cu(C10)_2$ in 4000–500 cm$^{-1}$ at room temperature.

one heat absorption is measured in all cases. The rest of the studied samples show differences between first and second heatings: an endothermic peak, sometimes followed by an exothermic one, is observed prior to the main heat absorption corresponding to the crystal–mesophase transition which occurs in the 373–383 K range.

The structural changes taking place at temperatures corresponding to those heat absorptions can be followed by examination of the IR spectra of the salts. Vibrational spectra at room temperature (Fig. 3) follow a similar pattern to that observed in other metallic alkanoates [2, 4]: bands ascribed to local modes (symmetric and asymmetric $COO^-$ stretchings, $CH_3$ stretchings and bendings, etc.) and bands characteristic of the polymethylenic chain are present. However, some important features must be remarked: the $CH_2$ wagging and twisting progression bands appearing in the 1300–1100 cm$^{-1}$ range are less regular than could be expected for compounds with a long alkyl chain. This fact must be related with the structure of the alkyl chain in these soaps. According to X-ray results available for n-decanoate, octanoate and butyrate [8–10], crystals of these compounds contain centrosymmetric dimers of general formula $(Cu(Cn)_2)_2$ with four hydrocarbon chains, two of which are rigorously all *trans* but the other two include

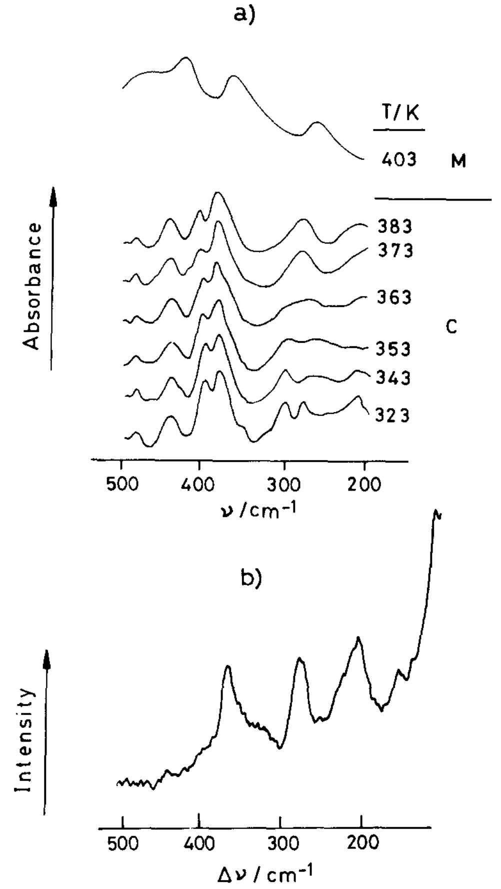

Fig. 4. Infrared (a) and Raman (b) spectra of Cu(C10)$_2$ in the low frequency region (C, crystal; M, mesophase).

*gauche* bonds near the carboxylic group. Each copper ion is surrounded by four oxygens of its dimer and one oxygen atom corresponding to the adjacent dimeric structure.

X-ray results also indicate that these compounds have a central core with a $D_{4h}$ centrosymmetric structure. Since that, four infrared ($2A_{2u}$ and $2E_{2u}$) and six Raman ($2A_{1g}$, $2E_g$, $B_{1g}$ and $B_{2g}$) active vibrations, in which Cu–O stretching and OCuO bending would be involved, should be observed in the low frequency region. Although the presence of the alkyl chains could modify the symmetry of the central core, the centrosymmetric geometry seems to remain as no coincidences between infrared bands and those observed in the low frequency Raman spectra are observed (see Fig. 4 and Table 1).

X-ray data for Cu(II) decanoate and octanoate [8] show that the dimers are arranged in the crystal in a triclinic subcell. This fact is evidenced in the infrared spectra by the absence of factor group splitting in the infrared $CH_2$ rocking an bending bands at about 720 and 1465 cm$^{-1}$, respectively. This absence is evident in all of the studied copper soaps showing that the triclinic subcell seems to be common to all these compounds.

In the crystal the asymmetric and symmetric carboxylate stretching modes appear at 1588 and 1416 cm$^{-1}$, respectively. These values are in agreement with a bridging bidentate structure for the carboxylate group as indicated by X-ray results [12].

When the temperature is increased some changes are observed in the infrared spectra. As an example Fig. 5 shows the evolution with temperature of the IR spectra of Cu(C10)$_2$. Noticeable changes in wave numbers of bands corresponding to $CH_2$ and $COO^-$ vibrations are observed. Wave numbers of $CH_2$ symmetric and $COO^-$ asymmetric stretching bands in Cu(C10)$_2$ are plotted against temperature in Fig. 6. As can be seen significant variations are observed in the crystal to the mesophase transition but in

Table 1. Vibrational spectrum of copper(II) dodecanoate in the range 400–100 cm$^{-1}$. Assignment follows the one proposed by Mathey *et al.* [11]

| Raman | IR ($\nu$/cm$^{-1}$) | | |
|---|---|---|---|
| ($\nu$/cm$^{-1}$) | 295 K | 383 K | Assignment |
| 105 | | | δ(Cu-Cu-O) |
| 152 | | | δ(Cu-CU-O) |
| 275 | | | δ(O-Cu-O) |
| | 279 | 283 | δ(O-Cu-O) |
| | 303 | | |
| | | 358 | ν(Cu-O) |
| 365 | | | ν(Cu-O) |
| | 383 | | ν(Cu-O) |
| | 398 | | ν(Cu-O) |

addition changes in wave numbers of the carboxylate stretching vibration are also observed in the temperature range prior to the mesophase where heat absorption is observed in the DTA curves. At the temperature of the crystal to mesophase transition some other important changes occur: the weak bands ascribed to rocking (1000–720 cm$^{-1}$) progression and those assignable to twisting and wagging progressions (1300–1100 cm$^{-1}$) disappear at that temperature (Fig. 5), pointing to drastic changes in the conformation of the alkyl chains which from this point would rotate almost freely. Moreover at the same temperature (Fig. 4), the low frequency infrared spectrum changes indicating that some modifications on the surroundings of the central core take place in the mesophase transition. Results of Giroud-Godquin *et al.* [13, 14] also suggest that a rearrangement which retains the binuclear structure occurs at this phase transition.

Apart from the changes in the frequency of carboxylate asymmetric (about 1600 cm$^{-1}$) and symmetric (about 1400 cm$^{-1}$) stretching modes mentioned before, significant variations occur in the bands corresponding to COO$^-$ wagging in a range of temperature before the mesophase. As an example Fig. 7(a) shows the spectrum of this band in copper decanoate. Only one band assignable to this vibration is observed around 587 cm$^{-1}$ at room temperature while two bands at 590 and 620 cm$^{-1}$ remain from 358 K up to the temperature corresponding to the solid–mesophase transition. Zerbi *et al.* [15]

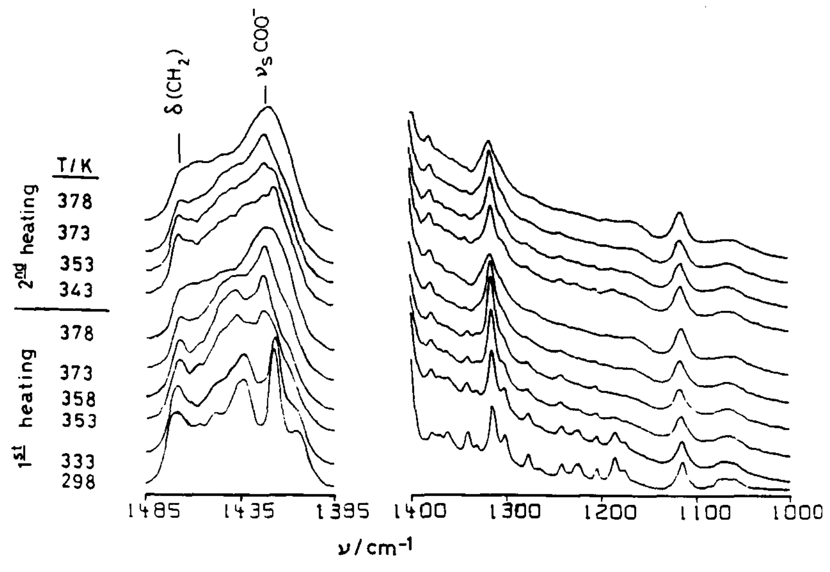

Fig. 5. Infrared spectra of copper(II) deconoate at different temperatures. A different ordinate scale has been chosen in each region. Each spectrum has been shifted vertically.

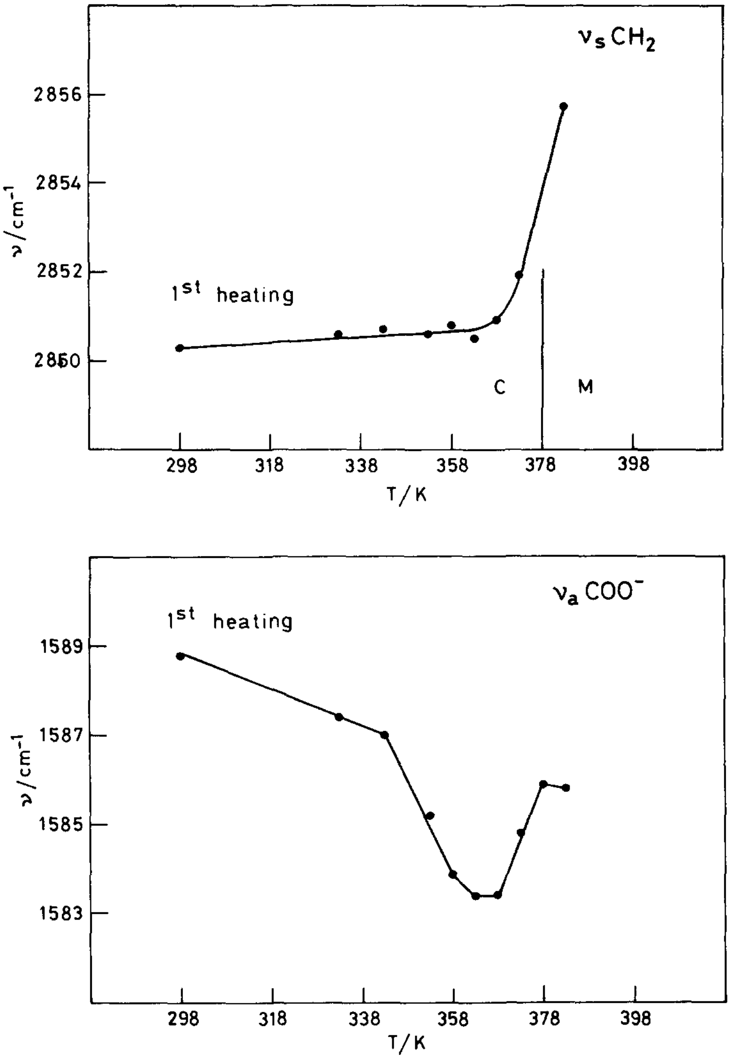

Fig. 6. Wave numbers of $CH_2$ symmetric and $COO^-$ asymmetric stretching bands of $Cu(ClO)_2$ plotted against temperature.

pointed out that $COO^-$ wagging vibration is very sensitive to the conformation of the alkyl chain with respect to the carboxylate group. According to their calculations this vibration is located around 550 $cm^{-1}$ when both are coplanar and shifts to 620 $cm^{-1}$ when the carboxylate and the alkyl chain are perpendicular. Some of the recrystallized samples have only one of these conformations and reorganization around the polar head group takes place when heating the sample (Fig. 7(a)). This conformational reorganization is observed as heat absorption prior to the transition to the mesophase in the DTA curves. This interpretation agrees with the fact that in $Cu(C11)_2$, where no heat absorption prior to the transition to the mesophase is observed, the two bands around 620 and 590 $cm^{-1}$ are present in the spectra of the crystal at room temperature (Fig. 7(b)), indicating that the reorganization around the polar group is already present in the crystal from that temperature.

In summary, IR results suggest that important structural modifications occur in $Cu(Cn)_2$ salts in the crystal–mesophase transition: the first one is related to alterations in the stacking of the binuclear complexes and is proved by the changes observed in the low frequency infrared spectra at the mesophase transition temperature (Fig. 4). The second one concerns the conformational changes in the alkyl chains which in the mesophase are disordered as in the liquid. Because of this the wave numbers of vibrational modes in

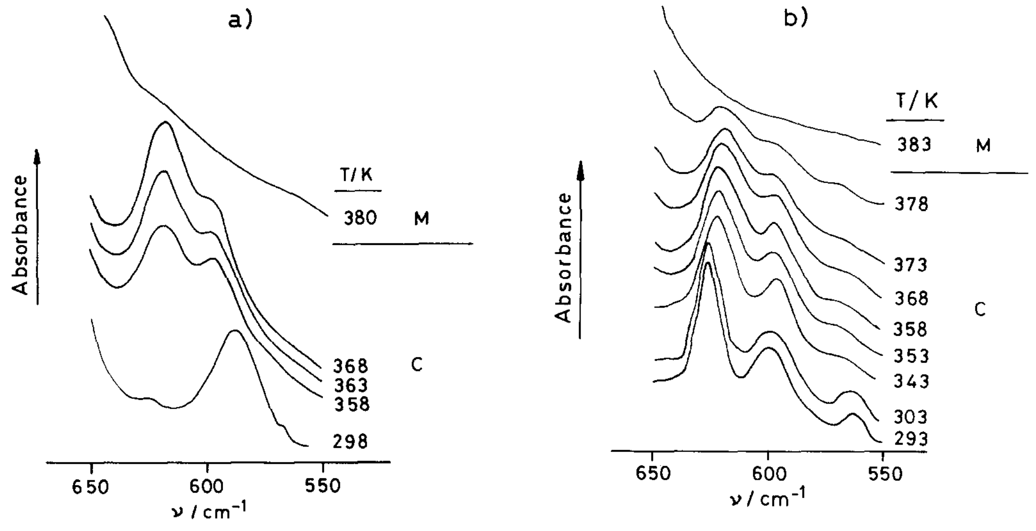

Fig. 7. Infrared spectrum of (a) $Cu(C10)_2$ and (b) $Cu(C11)_2$ in the 700–500 cm$^{-1}$ range.

which $CH_2$ and $CH_3$ groups are involved change noticeably (Fig. 6) and, at the same time, $CH_2$ wagging progression bands disappear (Fig. 4).

Some samples show a heat absorption prior to the crystal–mesophase transition (premelting phenomena) (Fig. 1). Since important changes in $COO^-$ wagging bands and in wave numbers of all $COO^-$ vibrations take place in these samples at the same range of temperatures, heat absorption must be related to changes in the local conformations around the $C_1$–$C_2$ bond. In the samples where these reorganizations are already present from the crystal no premelting phenomena are observed.

This behaviour is related to the capability of these compounds to adopt different forms (polymorphism) at room temperature, similar to that observed in fatty acids [15, 16].

*Acknowledgements*—The authors gratefully acknowledge the financial support provided by the Spanish DGCYT (Project number PB88-127). The facilities given by the Spectroscopy Service of the UCM for use of the Raman instrument are also acknowledged.

## REFERENCES

[1] M. S. Akanni, E. K. Okoh, H. D. Burrows and H. E. Ellis, *Thermochim. Acta* **208**, 1 (1992).
[2] M. V. García, M. I. Redondo, F. L. López de la Fuente, J. A. R. Cheda, E. F. Westrum Jr and F. Fernández-Martín, *Appl. Spectrosc.*, **48**, 338 (1994).
[3] J. A. R. Cheda, *J. Chem. Thermodyn.* **19**, 1261 (1987).
[4] M. V. García, M. I. Redondo and J. A. R. Cheda, *Vibr. Spectrosc.* **6**, 301 (1994).
[5] M. Ibn-Elhas, D. Guillon, A. Skoulios, A. M. Giroud-Godquin and P. Maldivi, *Liquid Crystals* **11**, 731 (1992) and references cited therein.
[6] H. Abied, D. Guillon, A. Skoulios, P. Weber, A. Giroud-Godquin and J. C. Marchon, *Liquid Crystals* **2**, 269 (1987).
[7] M. Yürekli, *Chim. Acta Turc.* **17**, 97 (1989).
[8] (a) T. R. Lomer and K. Perera, *Acta Crystallogr.* **B30**, 2912 (1974); (b) **B30**, 2913.
[9] M. J. Bird and T. R. Lomer, *Acta Crystallogr.* **B28**, 242 (1972).
[10] G. C. Campbell and J. F. Haw, *Inorg. Chem.* **27**, 3706 (1988).
[11] Y. Mathey, D. R. Greig and D. F. Shriver, *Inorg. Chem.* **21**, 3409 (1982).
[12] J. D. Donaldson, J. F. Knifton and S. D. Ross, *Spectrochim. Acta* **20**, 847 (1964).
[13] A. M. Giroud-Godquin, J. M. Latour and J. C. Marchon, *Inorg. Chem.* **24**, 4454 (1985).
[14] A. M. Giroud-Godquin, J. C. Marchon, D. Guillon and A. Skoulios, *Phys. Lett.* **45**, L681 (1984).
[15] G. Zerbi, G. Minoni and A. P. Tulloch, *J. Chem. Phys.* **78**(10), 5353 (1983).
[16] M. Kobayashi, F. Kaneko, K. Sato and M. Susuki, *J. Phys. Chem.* **90**, 6371 (1986).