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Vibrational studies of some dicopper tetracarboxylates which exhibit a thermotropic columnar mesophase

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Vibrational studies of some dicopper tetracarboxylates which exhibit a thermotropic columnar mesophase

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Infrared spectra have been obtained for a series of copper alkanoate dimers which include the caproate (dicopper tetrahexanoate), pelargonate (nonanoate), undecanoate, laurate (dodecanoate), palmitate (hexadecanoate) and docosanoate. Band assignments have been made wherever possible through the use of isotopic substitution, temperature studies and, in part, by Raman spectra. The results indicate that it should be possible to follow phase changes to the respective columnar mesophases of these complexes by monitoring the position of the methylene stretching frequency.

1. Introduction

It has been shown recently that binuclear complexes of fatty acids with transition metals such as copper(II) or rhodium(II) exhibit liquid-crystalline phases of the columnar type above 120°C [1, 2]. These molecules appear to exist in the mesophase as binuclear units (cf. figure 1) which stack above one another in columns of indeterminate length; in turn, these columns lie at the nodes of a two-dimensional hexagonal lattice. This type of mesophase is structurally identical to the so-called discotic mesophases exhibited by disk-like molecules such as the hexa-substituted derivatives of benzene [3] and triphenylene [4, 5] as well as the more closely related bis(3,4-nonyloxybenzoyl)methanatocopper(II) [6].

The solid state structures of three binuclear copper(II) alkanoates (butyrate, octanoate, and decanoate) have been determined from X-ray diffraction data by Lomer *et al.* [7–9]. It has been found that at least two gauche bonds are present in the alkyl chains of each of the three complexes. Thus, while two of the chains are rigorously all-trans, the other two are bent in such a fashion as to increase the packing efficiency. The resulting lattice has a lamellar structure, with layers of polar cores separated by two layers of paraffinic chains. It is not unreasonable to expect this behaviour to continue throughout the higher members of the series; indeed recent structural studies [1] have shown that the same type of lamellar lattice which has been fully characterized for the decanoate [7] is also found in the homologous complexes with $n = 12$ to $n = 22$ (n being even and equal to the number of carbon atoms in the corresponding fatty acid). The liquid-crystalline phases which appear upon heating,

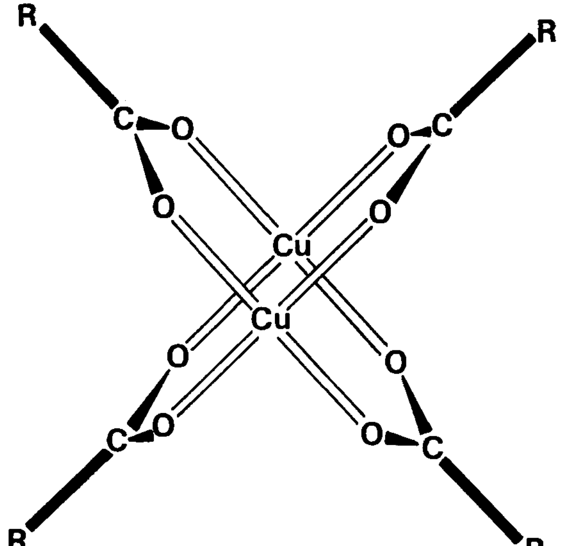

Figure 1. Schematic representation of the binuclear core of the copper alkanoates (R = *n*-alkyl).

generally exhibit disordered aliphatic chains with a number of gauche bonds higher than in the crystalline state [10]. Accordingly, in the study of copper(II) dodecanoate it was observed that the discotic mesophase is characterized by a columnar repeat distance of 20 Å, whereas 38 Å would be expected if the chains were fully extended [11].

The significance of these compounds lies in their potential as one-dimensional conductors or molecular ferromagnets. This, of course, has aroused considerable interest in their preparation and characterization. In this laboratory alone, more than 15 metal complexes of this type have been prepared and studied. One of our current goals is to improve our understanding of the nature of the molecular structure and of the bonding in the mesophase; that is to say we are attempting to gain an understanding of both inter- and intra-molecular interactions.

We have chosen to employ vibrational spectroscopy for our studies since it offers at the outset a direct probe of both the inter- and intra-molecular interactions. Changes in conformation and configuration of bonds affect local dipole moments whose changes during the execution of a normal mode are responsible for the observed infrared absorptions. Indeed, the power of this technique has been elegantly demonstrated by Casal *et al.* [12] in their study of n-$C_{10}H_{21}NH_3Cl$ and $(n\text{-}C_{10}H_{21}NH_3)_2CdCl_4$. They were able to monitor order–disorder transitions by following the frequency shifts of the ν (CH_2) mode as well as the W_2 component of the CH_2 wagging progression.

The use of Raman spectroscopy has been quite successful in elucidating the interactions in systems such as the benzene hexa-*n*-alkanoates [13]. In this study, it was concluded that the effective polarizability of the polymethylene sequences is an important factor in the stabilization of the mesophases. In fact, the one member in the series of compounds that they investigated which did not give a mesophase, namely benzene hexa-*n*-hexanoate, had a highly disordered polymethylene chain.

Clearly it is of the utmost importance to have dependable band assignments for these copper alkanoates in order to be able to relate the observed spectral changes to the dynamics within the mesophase, including those which occur in the molecular core. Thus the body of this paper presents the infrared spectra of a number of alkanoates together with the proposed assignments. The compounds studied include the caproate, pelargonate, undecanoate, laurate, palmitate and docosanoate copper dimers. In addition, Raman spectra were obtained for the laurate complex in the low frequency region. Fortunately, the infrared spectral properties of aliphatic monocarboxylic acids are well documented and thus present a convenient starting point for assigning the chain modes [14–16]. Similarly, the extremely detailed infrared and Raman study of the copper acetate dimer done by Mathey *et al.* identifies some of the most important core frequencies [17].

2. Experimental

The experimental procedure for the preparation of the compounds has been reported elsewhere [1] with the exception of the copper-65 laurate which was prepared by the direct reaction of copper-65 with lauric acid at 120–130°C for 2 hours. The compounds were subsequently purified by recrystallization from *n*-heptane and finally analysed for C, H and Cu in order to ascertain their purity. Copper-63 was obtained from Oak Ridge National Laboratories, Oak Ridge, Tennessee as the chloride, while the copper-65 was obtained as the metal from the Commissariat à l'Energie Atomique, 91190 Gif sur Yvette, France.

Infrared spectra were recorded using a dispersive instrument, the Beckman 4250, as well as interferometrically using a Nicolet 170SX FTIR. The samples were mounted as potassium bromide and caesium iodide pellets and as Nujol mulls on caesium iodide plates. Band positions were identical, within experimental error; however band intensities and baselines tended to vary depending upon the type of mounting procedure. Infrared spectra at elevated temperatures were obtained with a heated sample cell (SPECAC P/N 15-600 with a P/N 20-600 solid sample cell). In this case, the samples were run on a gold grid (196 mesh/cm^2) and on a gold grid mounted on a single potassium bromide plate.

Raman spectra were produced with the 5145 Å line of a Spectra Physics 164 Argon-ion laser. The samples were spun to avoid local heating effects and scattered radiation (90°) was collected and dispersed with a Dilor RTI equipped with a RCA C31034 photomultiplier tube. Amplification in the DC mode was accomplished with a Dilor 1830 DL.

3. Results and discussion

The infrared spectrum of the copper laurate dimer is illustrated in figure 2 and will serve as a point of reference throughout this discussion. It was obtained from a caesium iodide pellet and recorded using FTIR. Discussion of this compound as well as the others in the series is facilitated by subdividing the spectra into five separate regions. All of the compounds are assumed to have a regular core which belongs to the symmetry group D_{4h} and is represented by that in figure 1. This contention is consistent with the observation that the rule of mutual exclusion is obeyed in the low frequency range ($< 420\,\text{cm}^{-1}$) for those compounds which were studied by both infrared and Raman techniques. The justifications for the assignments, which are summarized in the table, are now given.

3.1. *3000–1600 cm^{-1}*

The methyl and methylene stretching modes which give rise to bands in this region are well-known [18] and indeed there is nothing surprising in any of the spectra.

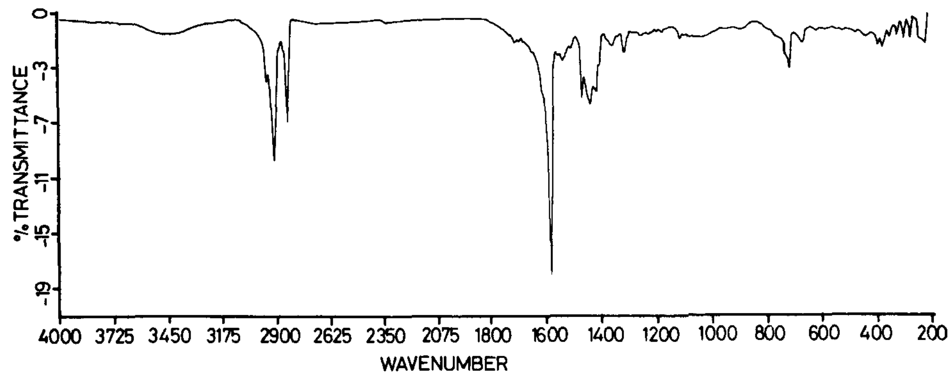

Figure 2. Infrared spectrum of copper laurate (4000–200 cm^{-1}) at room temperature.

Infrared absorptions (in cm^{-1}) of binuclear copper(II) alkanoates† and proposed assignments.

n						
6	9	11	12	16	22	Assignment
2952	2954	2955	2954	2952	2954	$\nu_{asym(CH_3)}$
	2918	2918	2915	2915	2915	$\nu_{asym(CH_2)}$
2870	2872	2872	2873	2873	2875	$\nu_{sym(CH_3)}$
2852	2850	2850	2849	2849	2849	$\nu_{sym(CH_2)}$
1587	1587	1586	1587	1585	1587	$\nu_{asym(COO)}$
1508	1508	1510	1501	1512	1513	?
—	—	—	—	1472	1473	$\delta_{(CH_2)\,def}$
1467	1467	1468	1469	1468	—	$\delta_{asym(CH_3)\,def}$
1415	1416	1416	1417	1416	1415	$\nu_{sym(COO)}$
1377	1378		1378	1376	1375	$\delta_{sym(CH_3)\,def}$
1311	1314	1313	1316	1318	1317	$\delta_{(CH_2)\,wag}$
1111	1113	1113	1115	1117	1114	$\delta_{(CH_3)\,def}$
724	721	722	(721) (733)	(721) (741)	716	$\varrho_{(CH_2)}$
664	666	668	672	672	670	$\delta_{(COO)}$
383	401	393	385	393	391	$\nu_{Cu\text{–}O}$

† *n* is the number of carbon atoms in the corresponding fatty acid.

However, in preliminary temperature studies which were conducted on the docosanoate complex (m.p. 118°C), we observed that the asymmetric stretch of the CH_2 moiety shifted by 8·6 cm^{-1} from 2914·6 to 2923·1 cm^{-1} as the temperature was increased from 36 to *c.* 140°C. Thus it appears that it will be possible to follow phase changes which involve conformational melting of the alkyl chains by careful temperature studies of this spectral region. Indeed, Casal *et al.* [12] were able to see this type of behaviour quite clearly in their solid state studies of $n\text{-}C_{10}H_{21}NH_3Cl$ and $(n\text{-}C_{10}H_{21}NH_3)_2CdCl_4$.

3.2. *1600–1300 cm⁻¹*

The bands in this interval result primarily from two different sources, the carboxyl groups and the methylene groups. The former give rise to two distinct bands which

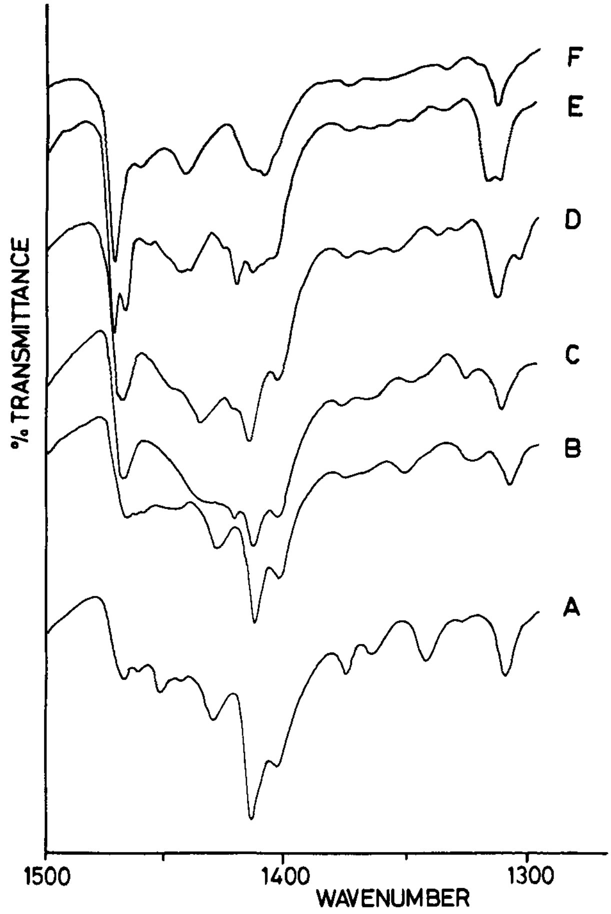

Figure 3. Expanded scale infrared spectra (1500–1300 cm^{-1}) of copper caproate (A), pelargonate (B), undecanoate (C), laurate (D), palmitate (E) and docosanoate (F).

can be described as $\nu_{as(C-O)}$ and $\nu_{sym(C-O)}$. The more intense of the two, $\nu_{as(C-O)}$, occurs at 1586 ± 1 cm^{-1} for all of the compounds which we have studied. Deacon and Phillips [19] concluded from a series of experiments on acetates and trifluoroacetates that for bridging complex, the difference between $\nu_{as(C-O)}$ and $\nu_{sym(C-O)}$ is close to that of the ionic species (164 cm^{-1}). In consequence we expect this mode to absorb at *c*. 1422 cm^{-1} and indeed there is a clearly defined band at 1415 cm^{-1} for each of the complexes (cf. figure 3). Although this is somewhat low for the $\nu_{sym(C-O)}$ of a bridged compound, we have chosen this band since it persists even in the melted form. It is important to recall, at this time, that these spectra were obtained as Nujol mulls as well as halide pellets. Both bands are clearly visible in the Nujol mulls and are found at the same positions as in the pellets. Thus there do not appear to be any pressure induced changes or halide coordination. These results are noteworthy in that they indicate that either the carboxyl moiety is quite insensitive to the strength of the Cu–O bond or that the Cu–O bond strengths are similar for each of the complexes.

In addition to the carbonyl stretching modes, we expect to find the CH_2 and CH_3 deformation bands in this region. A band at 1473 cm^{-1} is assigned as the CH_2 deformation while the asymmetric CH_3 deformation is observed at 1467 cm^{-1}. A weak band, observed at c. 1375 cm^{-1}, is assigned to the symmetric CH_3 deformation [18]. The justification for these choices can be clearly seen in figure 3 where, as the number of methylenes in the chain increases, the band at 1467 cm^{-1} begins to broaden, becomes a doublet for the palmitate and occurs at 1473 cm^{-1} for the docosanoate. Between 1400 and 1300 cm^{-1} only the band at 1311 cm^{-1} persists in the melts. Thus the others are tentatively assigned to coupled CH_2 deformation modes. The band at 1311 cm^{-1} is assigned to a methylene wagging mode. This mode has been observed previously in a study of the phase behaviour of solid *n*-alkanes [20]. It becomes a maximum in the melt and is presumed to be localized within a kink in the chain. The fact that we can observe this band before heating implies the existence of a structure of the type gauche–trans–gauche within the chains at room temperature. This, of course, is consistent with the X-ray results of the lower members of the series [7–9]. There is another medium strength band which always occurs between 1500 and 1515 cm^{-1}. We have no explanation for this band and merely report its position in each case.

3.3. *1300–1000 cm^{-1}*

It is in this region where the CH_2 wagging of long chain alkanes [14] and alkanoic acids [14, 15] are known to exhibit a series of sharp regularly spaced bands. The number of the bands and the complexity of the pattern increase as the number of methylene groups increases. Indeed, we might expect to be able to identify the various complexes by their band patterns, as has been done for the long chain alkanoic acids [15]. Unfortunately, the fact that two of the chains are bent complicates the situation and no clear pattern is evident. However, the increase in complexity with increasing chain length is clearly manifested in figure 4. The only band that persists in the melted form is observed at c. 1111–1115 cm^{-1} which we assign to another CH_3 deformation mode [21].

3.4. *1000–650 cm^{-1}*

It has been known for some time that the in-phase methylene rocking mode occurs at c. 724 ± 4 cm^{-1} in non-cyclic chains [22] and that the band is not observed unless there is a minimum of four consecutive all-trans methylene groups [23, 24]. This band is extremely sensitive to chain packing and splits into a doublet at c. 720 and 730 cm^{-1} when the polymethylene sequences are not equivalent [25]. Unfortunately, in a recent thermochemical study of copper carboxylates this band was mis-assigned as the COO bending mode [26] which, in reality, is observed at c. 670 cm^{-1}. We observe a strong band at 720 ± 4 cm^{-1} which is quite broad for the lower members of the series, is split for the laurate and palmitate and reaches a maximum in absorbance for the docosanoate. These observations are again in agreement with the conclusion from the X-ray data of the butyrate, octanoate and decanoate that two of the chains are bent. In a temperature study of the docosanoate, this band was observed to increase in intensity as the temperature is increased, indicating that it is indeed the CH_2 rocking mode.

We observe a second strong band in the spectra of each of the complexes at 670–690 cm^{-1} which we attribute to the COO bending mode. This value is close to that previously reported for the acetate ion and its sodium salt [27].

3.5. *650–200 cm^{-1}*

Early in this paper, it was stated that the rule of mutual exclusion was obeyed below 420 cm^{-1}. Figure 5, which shows the infrared absorption in this region for

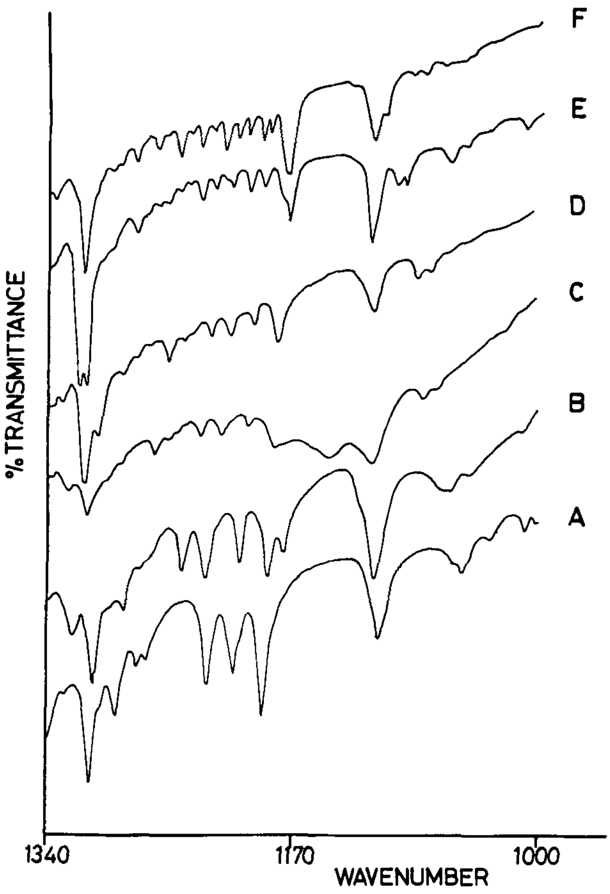

Figure 4. Expanded scale infrared spectra (1340–1000 cm^{-1}) of copper caproate (A), pelargonate (B), undecanoate (C), laurate (D), palmitate (E) and docosanoate (F).

copper laurate as well as the Raman lines for the same complex, is presented as evidence for this conclusion. Our aim at this point is to identify those vibrational modes which are related to the ligand and those which may be attributed to the core, i.e. the Cu–O stretches. Figure 6 shows the infrared absorptions from 650–300 cm^{-1} for the laurate complexes prepared with the isotopes copper-63 and copper-65 as well as the spectrum of the rhodium laurate. A number of conclusions may readily be made. The bands at 627, 601, 504 and 486 cm^{-1} are clearly related to the ligand since they do not shift on isotopic substitution and because the patterns are nearly the same as in the rhodium complex. The bands at 451 and 403 cm^{-1} also remain constant under isotopic substitution and have counterparts, though somewhat shifted, for the rhodium complex. However, the asymmetric band found at *c*. 385 cm^{-1} becomes more symmetric and shifts to lower frequency when copper-65 is substituted for copper-63. Furthermore, the intensity of this band relative to the band at *c*. 403 cm^{-1} diminishes drastically for the spectrum of the rhodium complex and a new strong band appears at 352 cm^{-1}. The latter is probably due to the Rh–O stretch of the same symmetry as the Cu–O stretch which we now assign at 385 cm^{-1} (band maximum observed in the complex when prepared with natural abundance copper). The low frequency spectra (420–230 cm^{-1}) of all of the complexes are presented in figure 7. There are no clear

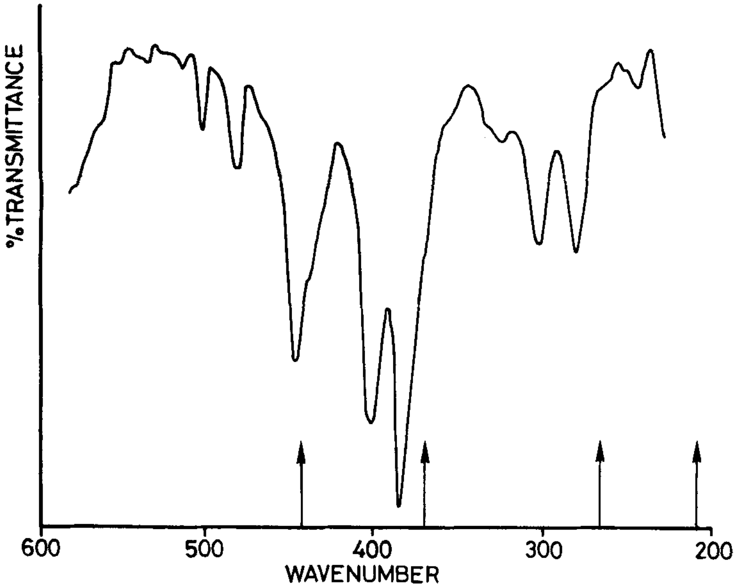

Figure 5. Infrared and Raman spectra of copper laurate (600–200 cm^{-1}). Arrows indicate the positions of the Raman bands.

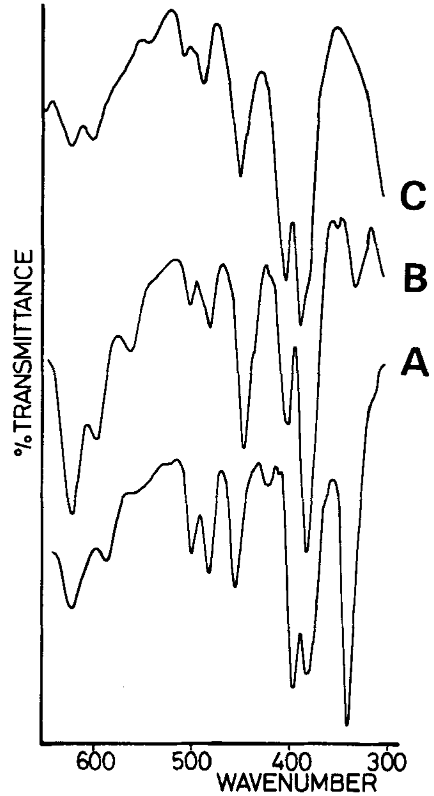

Figure 6. Infrared spectra (650–300 cm^{-1}) of (A) rhodium laurate, (B) copper-65 laurate and (C) copper-63 laurate.

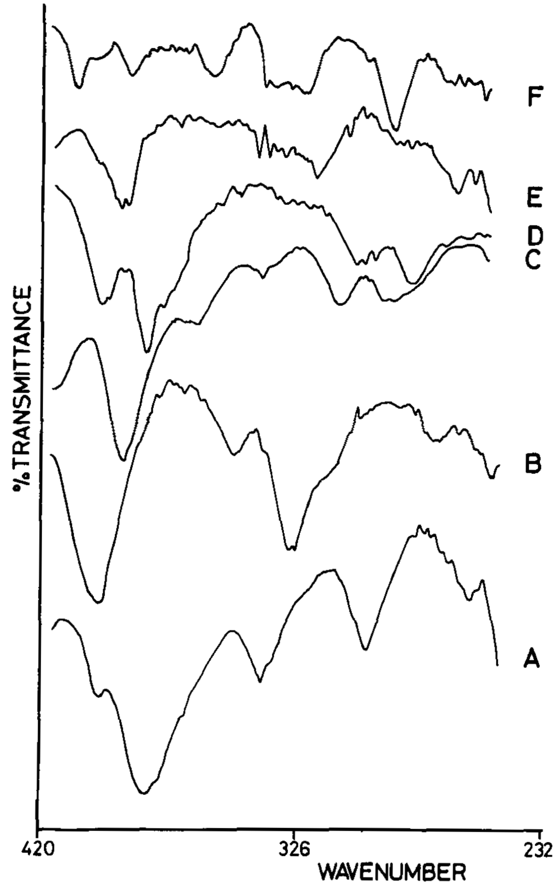

Figure 7. Expanded scale infrared spectra (420–220 cm^{-1}) of copper caproate (A), pelargonate (B), undecanoate (C), laurate (D), palmitate (E) and docosanoate (F).

trends which are evident although each complex does have a rather strong absorption between 380 and 402 cm^{-1}. Since we have found one of the Cu–O stretches for the laurate at 385 cm^{-1}, we tentatively assign these bands to Cu–O stretching modes. We do this with reasonable confidence since a Cu–O stretch of copper acetate has been assigned by Mathey *et al.* [17] at 388 cm^{-1}, and in addition the $\nu_{(Cu-O)}$ of a series of short chain alkanoates shows isotopically sensitive bands in this same region [28]. One might expect the Raman spectra to be of value in assigning the Cu–O stretching modes; however these compounds are rather poor Raman scatterers. Nevertheless, we were able to obtain Raman spectra of the laurate and observed four bands in the low frequency region.

4. Conclusion

The thermotropic behaviour of binuclear copper(II) *n*-alkanoates has elicited interest recently, due to the peculiar columnar structure observed in their mesophase. The present study was undertaken to obtain dependable band assignments in the vibrational spectra of these complexes, in order to be able to detect structural changes in their cores, as well as in their paraffinic chains, at the phase transition.

Four main conclusions can be drawn from these experiments.

(1) It should be possible to follow the phase change to the columnar mesophase by monitoring the infrared vibration at *c.* 2920 cm^{-1}, associated with the CH_2 asymmetric stretch.

(2) A CH_2 wagging mode at 1310–1320 cm^{-1} is associated with a kink in the polymethylene chains of the complexes. This vibration already occurs at room temperature, and its intensity increases at higher temperatures in the mesophase.

(3) An in-phase CH_2 rocking mode at *c.* 720 cm^{-1} is broadened or split in a doublet at room temperature, consistent with non-equivalent alkyl chains in each complex.

(4) The Cu–O stretching mode can be assigned to the band at 385 cm^{-1} for copper laurate, on the basis of isotopic substitution studies. Each complex in the series has a rather strong absorption between 380 cm^{-1} and 402 cm^{-1}, which can be safely assigned to this mode.

It was concluded from an earlier magnetic susceptibility study of copper(II) *n*-alkanoates [29] that a slight reorganization of the coordination shell, which retains the binuclear structure of the complex, occurs at the solid–mesophase transition. Future studies will aim at detecting changes in the vibrations of the core at the phase transition, including those in metal–oxygen bonds of the copper complexes and those of the metal–metal bonds in the rhodium complexes and their 4*d* congeners [2].

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