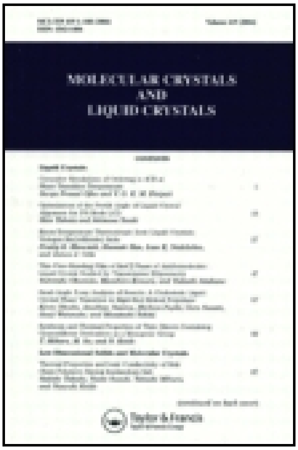


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Structural and Vibrational Study of the Phase Transitions in Crystalline bis(n-decylammonium)tetrachlorocuprate

N. B. Chanh [a] , C. Lartigue-bourdeau [a] , M. Khechoubi [a] , J. K. Kang [b] , J. H. Choy [b] & M. Rey-lafon [c]

[a] Laboratoire de Cristallographie et de Physique Cristalline, URA 144 CNRS, Université Bordeaux I, 33405, Talence, France

[b] Department of Chemistry, Seoul National University, Seoul, 151-742, Korea

[c] Laboratoire de Spectroscopie Moléculaire et Cristalline, URA 124 CNRS, Université Bordeaux I, 33405, Talence, France

To cite this article: N. B. Chanh , C. Lartigue-bourdeau , M. Khechoubi , J. K. Kang , J. H. Choy & M. Rey-lafon (1994): Structural and Vibrational Study of the Phase Transitions in Crystalline bis(n-decylammonium)tetrachlorocuprate, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 238:1, 93-108

To link to this article: http://dx.doi.org/10.1080/10587259408046918

Mol. Cryst. Liq. Cryst., 1994, Vol. 238, pp. 93–108
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Structural and Vibrational Study of the Phase Transitions in Crystalline bis(*n*-decylammonium)tetrachlorocuprate

N. B. CHANH, C. LARTIGUE-BOURDEAU and M. KHECHOUBI

Laboratoire de Cristallographie et de Physique Cristalline, URA 144 CNRS, Université Bordeaux I
33405 Talence, France

and

J. K. KANG and J. H. CHOY

Department of Chemistry, Seoul National University, Seoul 151-742, Korea

and

M. REY-LAFON

Laboratoire de Spectroscopie Moléculaire et Cristalline, URA 124 CNRS, Université Bordeaux I
33405-Talence, France

(Received February 9, 1993)

Five crystalline phases have been characterized in the perovskite layer compound $(C_{10}H_{21}NH_3)_2CuCl_4$, using differential scanning calorimetry, X-ray diffraction and infrared spectroscopy. The ordered phase V contains three types of hydrocarbon chains; two of them have an almost extended configuration with a gauche bond in the proximity of the NH_3 group, the other one is the planar all-trans form. The proportion of the different forms varies as a function of temperature from 100 K to 306 K within phase V. The crystallographic symmetry of phases V and IV is triclinic while phases II and I belong to the monoclinic and orthorhombic systems respectively. When raising temperature, two discontinuous transitions, V-III and III-II, affect the interlayer distances and are related to the presence of conformational defects of the type gt^3g^- and gtg^-, respectively, as well as to a relative disorder in the chain orientations. When decoupling the III-V transition by cooling, the abrupt change in the lattice parameters occurs between phases III and IV. The high temperature II-I transition is athermic and implies only a continuous structural modification from the monoclinic to the orthorhombic symmetry.

Keywords: Bidimensional compounds, phase transitions, conformational disorder, X-ray diffraction, Infrared spectroscopy

INTRODUCTION

Perovskite-type layer compounds of general formula $(C_nH_{2n+1}NH_3)_2MCl_4$ (CnM for short) show a large variety of order-disorder structural phase transitions which are governed by the dynamics of the alkylammonium groups and by the rotational motions of the MCl_4 macroanions about their crystallographic axes. The type of disorder which can occur and the sequence of thermotropic phase transitions depend on several factors. For compounds containing the same alkylammonium cation, it depends on the nature of the metal ion but the reason of this effect is not well understood.

When M = Cd, Mn, Cu, the mineral layers are constituted of more or less distorted corner-sharing MCl_6 octahedra forming a two dimensional matrix and are sandwiched between hydrocarbon layers. The NH_3 groups are attached to the layers by weak NH . . . Cl hydrogen bonds. Van der Waals interactions and long range Coulomb forces account for the interlayer bonding. Crystalline structure and phase sequence above room temperature of C10Cd are well known.[1] The chains are tilted by 40° with respect to the layer normal and form a zig-zag arrangement along the crystal c axis. This compound exhibits two first order phase changes, a minor one at 308 K and the main one at 312 K. The first transition is related to the onset of a reorientational motion of the chain heads between two positions in the cavities, accompanied by a beginning of melting; the second one corresponds to the occurrence of an important conformational disorder.[1,2] In the room temperature (RT) phase of C10Mn, the chains are tilted by 45° and are all parallel to the same direction.[3] The unique phase change at 308 K, leads to a disorder similar to that of the high temperature (HT) phase of C10Cd.[4]

Neither the structure nor the space group of C10Cu are known; however it has been shown from X-ray diffraction diagrams that all the chains are tilted by 40° with respect to the layer normal and parallel to a single direction.[5] Though the geometry of the octahedral cavities has not been described, one can admit that it resembles the structure of the inorganic part of the homologous compound $(C_3H_7NH_3)_2CuCl_4$[6]: the copper and chlorine atoms form square planar $CuCl_4^{2-}$ ions with Cu—Cl bonds of 2.29 Å bound together in sheets nearly perpendicular to the planes of $CuCl_4^{2-}$ ions by Cu—Cl bonds of 3.04 Å. Consequently, the octahedral configuration of the copper atoms is distorted. Using infrared spectroscopy, we have shown in a recent study[7] that three types of chain conformations are present at room temperature. This is different from C10Cd which contains equal proportions of A (one gauche (g) bond between the first and the second carbon atoms) and B (one gauche bond between the second and the third carbon atoms) and from C10Mn where all the chains are in the B form.

C10Cu as C10Cd presents two successive phase changes at 309 K and 312 K, but their order is reversed[5,8,9]: it has been stated from DSC and ^{13}C NMR measurements that the first one implies only a conformational disordering and the second transition is due to a disordering of the polar heads.[5,8] But our study indicates that both processes in C10Cu are coupled and begin at the lower transition.[7]

In the present work, the crystallographic aspect of the polymorphic behavior of $(C_{10}H_{21}NH_3)_2CuCl_4$ has been studied by X-ray diffraction technique, on powdered samples. This analysis allowed the determination of the unit-cell parameters of most of the different encountered phases, in particular the higher temperature ones I and II and the lower temperature ones IV and V. The intermediate phase III, stable within a very narrow temperature range ($\Delta T \simeq$ 3–4 degrees), gives a diffraction pattern unable to permit an easy indexing tentative. However, X-ray diffraction alone cannot give complete information on the characteristic features of the phase transitions, in particular those concerning the dynamics of the chains and the way in which they are involved. To answer this type of question, we have performed a simultaneous infrared spectroscopic study.

EXPERIMENTAL

Diffraction experiments have been performed with a Guinier-Simon camera using the monochromatized radiation CuKα_1 (1.5406 Å). This technique allows to obtain a diffraction pattern which shows the continuous variation of all the diffraction lines with temperature. The geometry of the diffraction scheme was Seeman-Bohlin type. The experimental conditions were as follows: X-ray generator power of 1 Kw, window width of 1.0 mm, film speed of 1.5 mm.h^{-1}. In order to prevent eventual moisture effects during thermal variation on the sample (low temperature experiments) the powdered product was introduced and sealed in a Lindemann capillary of 0.5 mm diameter and then centered in the X-ray beam. The crystalline preferred orientation effects due to the formation of microcrystals (platelets) remained present in the sample in spite of a long grinding; they were minimized by rotating the capillary around its axis during the measurements. Evolution of the temperature was obtained using a nitrogen gas flow system and checked by a chromel-alumel thermocouple located near the sample. The temperature regulation was controlled by an electronic programmer for heating or cooling processes. The selected temperature range was 100–373 K and the rates of temperature variations were defined owing to the type of desired exploration: 0.1 K min^{-1}; 0.07 K min^{-1}; 0.027 K min^{-1}. The uncertainty of the temperature, determined from the diffraction pattern, was estimated to be ± 3 K: this accuracy depends of course on the sharpness of the diffraction pattern changes related to the corresponding phase transition. On the other hand, the positions of the diffraction lines were determined from the diffraction film by using a calibrated ruler (for λ = CuKα_1) which gives directly the corresponding distances d_{hkl}. In this technique, the accuracy in the determination of d_{hkl} depends on the θ regions: for instance, in low θ region, it is estimated to be 0.1 Å (at $d \simeq 10$ Å) and in high θ region, to be 0.003 Å (at $d \simeq 1.5$ Å). So, for fixed room temperature investigations, (phase V), a powder diffractometer allowing a very slow scanning speed of the detector (1/20°/2θ/min) was used to improve the accuracy of the positions of diffraction lines ($\pm 0.01°/\theta$). The results were then corrected for systematic errors by using an internal standard (quartz).

The phase transitions of $(C_{10}H_{21}NH_3)_2CuCl_4$ have also been investigated by differential scanning calorimetry (DSC). We have used a Perkin-Elmer Series 7 apparatus. The experimental conditions were: temperature range 293 K–353 K, heating or cooling rates 2 K min^{-1}, weight of sample 2–3 mg. The transition temperatures were defined according to ICTA (International Confederation of Thermal Analysis) recommendations: they were given as the "onset" temperature "T_0" (for first-order transitions) of the corresponding DSC signals. Peak temperatures "T_s" can also be usefully given in order to describe the sharpness of the thermal phenomenon. Let us recall that only T_s is considered for second-order transitions.

Polycrystalline films for the infrared measurements were prepared on CsI windows by rapid evaporation of hexane solutions. The spectra were registered using a Bruker 113V FTIR interferometer equipped with a MCT detector. The resolution was 1 cm^{-1} and 300 scans were accumulated. The samples were in an evacuated chamber where temperatures were stable within 1°C.

RESULTS

I. DSC Analysis

The results are given on Figure 1a (heating process) and Figure 1b (cooling process). On the heating curve, two endothermic signals are observed respectively at 309.3 K and 313.6 K ("onset" temperatures) and on the cooling curve, three exothermic signals are detected, respectively at 312.4 K, 309.0 K and 305.4 K. These phenom-

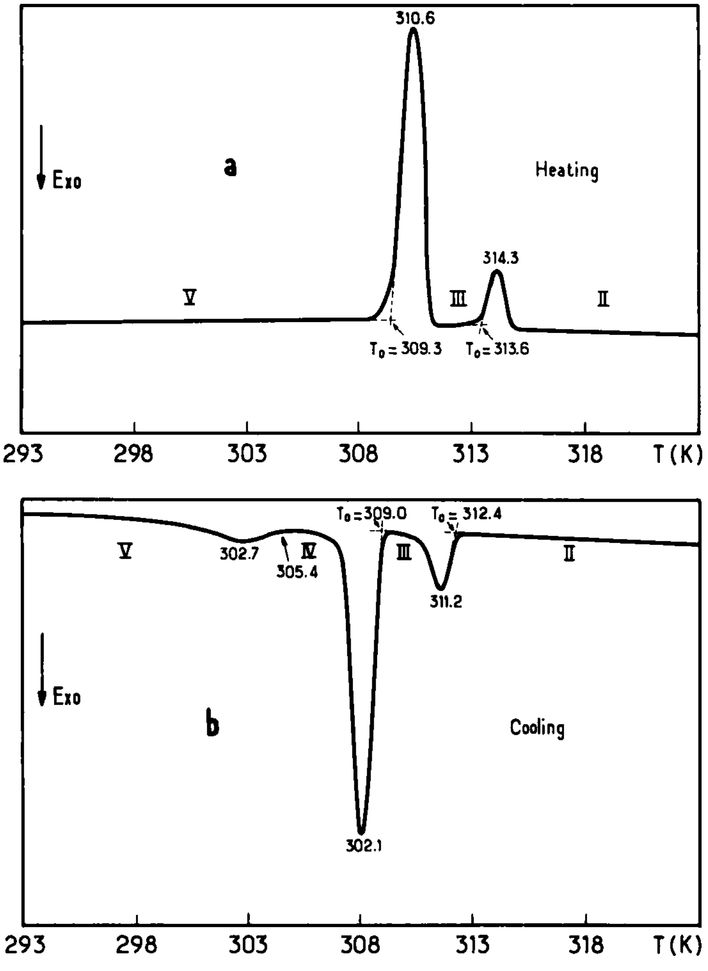


FIGURE 1 DSC results (2 K min^{-1}): a) Heating process; b) cooling process.

ena have already been pointed out in a precedent paper,[7] but some small differences can be observed in the temperature values: we think that these discrepancies can be due to the use of different calorimeters and probably to the ageing of the products. Nevertheless, these calorimetric results give evidence of four crystallographic phases of C10Cu.

II. X-ray Diffraction Results

1. Evidence of crystallographic phase transitions. In order to study the variations of the diffraction diagrams with the temperature through the different phase transitions in $(C_{10}H_{21}NH_3)_2$ $CuCl_4$, three experiments have been performed with the Guinier-Simon camera:

- a heating experiment in the low temperature region between 100 K–223 K, with a rate of 0.1 K min^{-1}.
- a heating experiment between 223 K and 343 K with a heating rate of 0.07 K min^{-1}.
- a cooling experiment from 373 K to 293 K, with a low cooling rate of 0.027 K min^{-1}.

The different temperature rates (heating or cooling) have been chosen in order to point out more easily the diffraction changes on the pattern. The transition temperatures observed by diffraction analysis are slightly different from those obtained by DSC analysis which has been performed with a higher temperature rate (2 K min^{-1}).

In the temperature range of 100 K–223 K (Figure 2), no clear crystalline phase change is observed on the pattern. This region corresponds to the low temperature phase of $(C_{10}H_{21}NH_3)_2$ $CuCl_4$ called phase V. Curvation of the diffraction lines towards low θ diffraction angles when the temperatures increases is only due to the thermal expansion of the unit-cell.

In the second diffraction pattern between 223 K and 343 K (Figure 3a), two main crystalline phase changes are detected at around 306 K and 310 K, respectively. These transitions correspond to a sudden increase of the interlayer distances d_{00l} between the perovskite sheets through two successive steps as it can be seen by the shifts of the first diffraction lines d_{00l} (1 = 4, 6, 8, 10) on the left of the film towards low θ angles when the temperature increases. These changes are sharply discontinuous and affect also the whole diffraction pattern. They certainly correspond to the phase transitions observed by DSC analysis at 309.3 K and 313.6 K, respectively. The distance d_{006}, equal to 8.4 Å for the room temperature phase

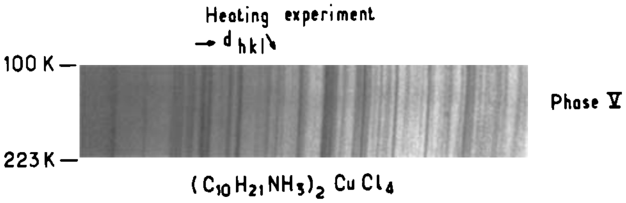
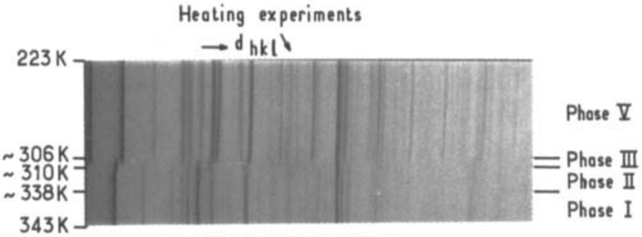
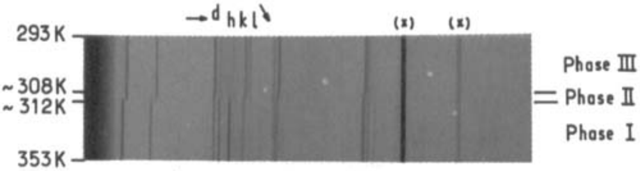


FIGURE 2 Guinier-Simon diffraction analysis at low temperature.



(a) $(C_{10}H_{21}NH_3)_2CuCl_4$



(b) $(C_{10}H_{21}NH_3)_2CdCl_4$

(x) lines of sample holder (Al)

FIGURE 3 Heating diffraction patterns: a) C10Cu (Guinier-Simon) temperature range 223–343 K; b) C10Cd (Guinier-Lenné) temperature range 293–353 K.

(V) becomes 9.0 Å in the intermediate phase (III) and is 9.2 Å in the upper phase (II). On this diffraction pattern, another change can be detected at higher temperature (≃338 K). It corresponds only to small modifications of some diffraction lines. In particular, several double lines, present immediately higher than 310 K, become progressively unique at ≃ 338 K. These minute changes could be attributed to a phase transition of second order type which does not affect the interlayer distance since the lines are continuous around 338 K. This progressive transition could correspond to a structural "monoclinic-orthorhombic" change of the structure with a small modification of the monoclinic angle which becomes equal to 90 degrees in the highest temperature phase. This assumption is supported by the similarity of the high temperature diagrams of the C10Cu and C10Cd (Figure 3b); indeed the structure of the cadmium derivative has been found to be orthorhombic.[1] So, we can propose the following crystallographic phase changes with increasing temperatures: V → III at ≃306 K; III → II at ≃310 K; II → I at ≃338 K. The last phase change (338 K) is not detected by DSC analysis.

On the cooling diffraction pattern (Figure 4), it can be pointed out that the three phase transitions cited above are reversible, with some delays. The corresponding temperatures, measured from the film, are respectively equal to 326 K, 309 K and 306 K. On the diffraction diagram, it can be seen another phase change at around 300 K. Such a very weak transition is detected by small modifications of some doublets which become unique at this temperature. Like the II ↔ I transition around 326 K, this transition does not modify the interlayer distance which shows no discontinuity when the temperature diminishes from 306 K to 293 K. However, this transition does not occur progressively, so that a small peak is detected at 302.7 K on the DSC thermogram.

In summary, Guinier-Simon diffraction analysis shows the existence of four phase

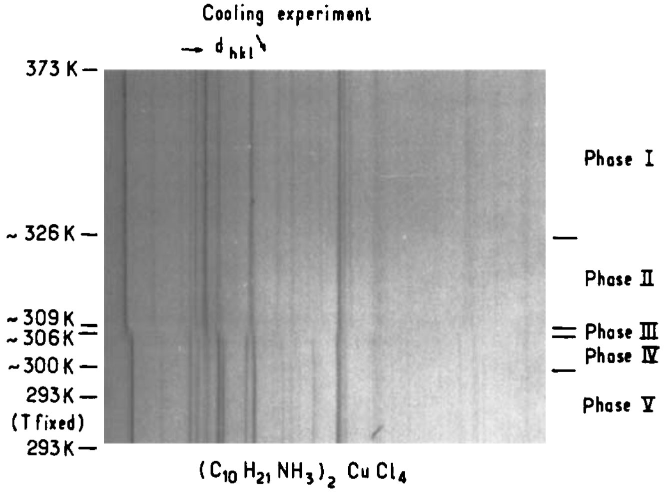


FIGURE 4 Guinier-Simon diffraction pattern obtained by cooling from 373 K to 293 K.

transitions in $(n\text{-}C_{10}H_{21}NH_3)_2\ CuCl_4$ crystals and consequently of five crystallographic phases named I, II, III, IV and V according to the following schemes.

V III II I

increasing temperature → T(K)

306 310 ~338

V IV III II I

decreasing temperature ← T(K)

300 306 309 ~326

2. *Crystallographic Analysis of the Different Phases.* Determination of the crystallographic unit-cell of the different phases in $(n\text{-}C_{10}H_{21}NH_3)_2\ CuCl_4$ has been done from the powder diffraction data, beginning by the phase I which shows numerous similarities with the known orthorhombic HT phase of C10Cd (Figures 3a and 3b).

a. Form I. The powder data have been measured at approximate temperature of 340 K in Guinier-Simon pattern. The analogies with the HT phase of C10Cd allow to index this powder diagram in the orthorhombic system. The refinement on the whole diffraction pattern (28 observed diffraction lines have been used) is then performed with a program named AFMAIL and leads to the results shown in Table I. After refinement, the parameters are obtained as follows:

Form I (340 K): orthorhombic
a = 7.261 (4) Å
b = 7.343 (4) Å
c = 54.65 (3) Å
Z = 4

TABLE I

X-ray (Guinier-Simon) powder data for the form I of $(C_{10}H_{21}NH_3)_2$ $CuCl_4$ ($T \sim 340$ K)

N°	θ_{obs}	h k l	θ_{calc}	$\theta_{obs}-\theta_{calc}$
1	3.250	0 0 4	3.232	0.018
2	4.850	0 0 6	4.851	-0.001
3	6.500	0 0 8	6.474	0.026
4	8.100	0 0 10	8.102	-0.002
5	8.575	1 1 0	8.580	-0.005
6	8.905	1 0 8	8.906	0.001
		and / or		
		1 1 3	8.920	-0.015
7	9.480	0 1 9	9.474	0.006
		and / or		
		1 1 5	9.497	-0.017
8	10.290	1 1 7	10.303	-0.013
9	12.090	0 2 0	12.110	-0.020
10	12.230	1 0 13	12.223	0.007
		and / or		
		2 0 0	12.249	-0.019
11	12.800	0 2 5	12.787	0.013
12	13.720	2 1 1	13.716	0.004
13	14.495	1 2 6	14.468	0.026
14	15.525	1 2 9	15.494	0.031
15	16.160	0 2 13	16.173	-0.013
16	17.110	1 1 18	17.116	-0.006
17	17.385	2 2 0	17.360	0.025
		and / or		
		2 2 1	17.380	0.005
18	17.455	2 2 2	17.440	0.015
19	17.700	2 2 4	17.678	0.022
20	17.885	1 2 14	17.874	0.011
21	19.065	2 1 16	19.081	-0.016
22	19.320	2 0 18	19.313	0.007
23	19.450	3 0 7	19.463	-0.013
		and / or		
		1 3 2	19.469	-0.019
24	19.760	0 0 24	19.771	-0.011
25	20.130	1 1 22	20.127	0.003
26	20.510	2 2 13	20.496	0.014
		and / or		
		1 3 8	20.531	-0.021
27	24.625	3 2 12	24.647	-0.022
28	26.295	4 0 9	26.288	0.007
		and / or		
		3 2 16	26.288	0.007

Differences between θ_{obs} and θ_{calc} are less than 0.03° which can be considered as acceptable for the refinement through this technique. In the case of C10Cd, Kind *et al.*[1] have proposed the Amaa group for the highest temperature phase and Schenk,[10] the Cmcm group. Examination of the possible values of hkl (Table I) shows that these groups are not compatible with the present results on our compound. On the other hand, Kind *et al.* have determined the intermediate temperature phase of C10Cd as Pmnn: this group seems compatible with the hkl indices

(Table I) for the phase I of C10Cu, though we cannot produce any clear evidence of such conclusions.

b. Form II. The measurements have been made on the diffraction pattern at a temperature immediately above $T = 310$ K. The fact that some unique lines of the orthorhombic high temperature form I (in particular the 113, 115 and 117 lines) become double leads to assign the form as monoclinic. 29 observed diffraction lines have been used for refinement of the unit-cell parameters. We have obtained:

Form II (T ~ 315 K): monoclinic
$a = 7.277$ (3) Å
$b = 7.293$ (3) Å
$c = 54.59$ (2) Å
$\beta = 92.25$ (4)°
$Z = 4$

Comparison between θ_{obs} and θ_{calc} is given in Table II: the differences are less than 0.03°, which can be considered as acceptable. The index hkl show that the results are compatible with $P2_1/a$ or $P2_1/n$ space groups. Let us recall that the RT phase of C10Cd belongs to the $P2_1/n$ space group.[1]

c. Form V. This form corresponds to the RT phase of C10Cu. A single crystal diffraction study has already been made by K. Schenk *et al.*[11] who have found the following parameters: triclinic symmetry, $P\bar{1}$, $a = 7.2490$ (6) Å; $b = 7.5740$ (9) Å; $c = 51.120$ (7) Å, $\alpha = 93.21$ (1)°; $\beta = 92.053$ (9)°; $\gamma = 90.013$ (8)°, $Z = 4$. From our powder Guinier-Simon data, completed with the results of powder diffractometer, the refinement of 30 observed lines has given the following unit-cell:

Form V (293 K) Triclinic
$a = 7.219$ (6) Å
$b = 7.509$ (7) Å
$c = 51.19$ (2) Å
$\alpha = 92.7$ (1)°
$\beta = 92.11$ (7)°
$\gamma = 89.86$ (5)°
$Z = 4$

Differences $|\theta_{obs} - \theta_{calc}|$ are less than 0.03° (Table III). Nevertheless, our results present small differences with the data of Schenk *et al.* They could be explained by the different origins of the products.

d. Form IV. The diffraction pattern of this form can be observed between 306 K and 300 K, during slow cooling X-ray experiment (Figure 4). The differences in the diffraction pattern between form V and form IV are little and no discontinuity is observed concerning the interlayer distance at the passage IV → V. Only some unique lines of form V (in particular at $\theta = 9.754°$ and 10.500° (Table III) become clearly double in form IV. These observations lead us to consider that form IV could have a triclinic symmetry as form V and we have refined the diffraction diagram of form IV with this assumption. The results are:

TABLE II

X-ray (Guinier-Simon) powder data for the form II of $(C_{10}H_{21}NH_3)_2\ CuCl_4$ (~315 K)

N°	θ_{obs}	h k l	θ_{calc}	$\theta_{obs}-\theta_{calc}$
1	3.250	0 0 4	3.238	0.012
2	4.850	0 0 6	4.859	-0.009
3	6.505	0 0 8	6.486	0.019
4	8.100	0 0 10	8.117	-0.013
5	8.575	1 1 0	8.603	-0.028
6	8.870	$\bar{1}$ 1 3	8.878	-0.008
7	9.030	1 1 3	9.009	0.020
8	9.440	$\bar{1}$ 1 5	9.417	0.022
9	9.650	1 1 5	9.624	0.024
10	10.185	$\bar{1}$ 1 7	10.194	-0.009
11	10.450	1 1 7	10.461	-0.011
12	11.400	0 0 14	11.401	-0.001
13	12.195	0 2 0	12.194	0.001
14	12.230	2 0 0	12.232	-0.002
15	12.950	0 0 14	12.951	-0.001
16	13.520	$\bar{1}$ 1 13	13.506	0.014
17	13.720	$\bar{2}$ 1 2	13.734	-0.014
		and / or		
		$\bar{1}$ 2 2	13.738	-0.018
		and / or		
		2 0 7	13.726	0.004
18	15.525	$\bar{1}$ 1 16	15.513	0.012
		and / or		
		2 0 11	15.520	-0.005
19	16.280	$\bar{1}$ 2 11	16.289	-0.009
20	17.180	2 0 14	17.180	-0.000
21	17.250	$\bar{1}$ 2 13	17.257	-0.007
22	17.455	2 2 1	17.441	0.013
23	17.815	2 2 4	17.818	-0.003
24	19.180	$\bar{1}$ 1 21	19.170	0.010
25	19.400	1 0 22	19.397	0.003
26	19.790	0 0 24	19.808	-0.017
27	21.300	2 2 14	21.293	0.007
28	23.160	$\bar{1}$ 3 15	23.162	-0.002
29	24.910	$\bar{3}$ 1 19	24.912	-0.002

Form IV (303 K) Triclinic
a = 7.21 (1) Å
b = 7.50 (1) Å
c = 51.19 (2) Å
α = 92.7 (1)°
β = 91.8 (1)°
γ = 89.6 (1)°
Z = 4

The comparison between θ_{obs} and θ_{calc} is given in Table IV. From a crystallographic point of view, the unit-cell of form IV is nearly the same as that of form

TABLE III

X-ray (automatic powder diffractometer) data for the form V of $(C_{10}H_{21}NH_3)_2\ CuCl_4$ (293 K)

N°	θ_{obs}	h k l	θ_{calc}	$\theta_{obs}-\theta_{calc}$
1	3.440	0 0 4	3.457	-0.017
2	5.203	0 0 6	5.203	0.013
3	6.918	0 0 8	6.927	-0.009
4	8.559	1 $\bar{1}$ 1	8.561	-0.002
5	8.567	$\bar{1}$ 1 1	8.572	-0.005
6	8.592	$\bar{1}$ $\bar{1}$ 2	8.591	0.001
7	8.889	1 $\bar{1}$ 3	8.899	-0.009
		and / or		
		0 $\bar{1}$ 8	8.899	-0.009
8	9.051	1 1 3	9.055	-0.004
9	9.420	1 0 8	9.439	-0.019
10	9.605	$\bar{1}$ 1 5	9.594	0.011
11	9.754	$\bar{1}$ 0 9	9.761	-0.007
12	10.255	1 1 6	10.256	-0.001
13	10.500	$\bar{1}$ 1 7	10.512	-0.012
14	11.341	1 1 8	11.329	-0.005
		and / or		
		1 0 11	11.567	-0.016
16	12.261	0 2 3	12.262	-0.001
17	12.330	$\bar{2}$ 0 1	12.330	0.000
		and / or		
		2 0 0	12.331	-0.001
18	13.385	1 2 0	13.382	0.003
		and / or		
		1 $\bar{2}$ 0	13.389	-0.004
19	14.029	1 2 4	14.038	-0.009
20	14.399	$\bar{1}$ $\bar{2}$ 7	14.399	0.000
		and / or		
		$\bar{2}$ 0 9	14.404	-0.005
21	14.890	$\bar{2}$ 0 10	14.882	0.008
		and / or		
		1 $\bar{1}$ 14	14.902	-0.012
		and / or		
		2 0 9	14.904	-0.014
22	15.725	$\bar{1}$ 1 15	15.730	-0.005
		and / or		
		0 0 18	15.745	-0.020
23	17.180	1 0 18	17.172	0.008
		and / or		
		1 $\bar{1}$ 17	17.174	0.006
24	17.247	2 $\bar{2}$ 0	17.242	0.005
		and / or		
		2 $\bar{2}$ 1	17.259	-0.012
25	17.385	$\bar{2}$ $\bar{2}$ 4	17.384	0.001
26	17.597	2 2 3	17.594	0.003
27	18.030	2 $\bar{2}$ 6	18.022	0.008
		and / or		
		0 $\bar{2}$ 16	18.023	0.007
		and / or		
		1 $\bar{2}$ 14	18.026	0.004
		and / or		
		2 $\bar{1}$ 13	18.029	0.001
28	19.390	0 0 22	19.370	0.020
29	21.218	0 0 24	21.211	0.007
30	23.099	0 0 26	23.077	0.022

TABLE IV

X-ray (Guinier-Simon) powder data for the form IV of $(C_{10}H_{21}NH_3)_2\ CuCl_4$

N°	θ_{obs}	h k l	θ_{calc}	$\theta_{obs}-\theta_{calc}$
1	3.450	0 0 4	3.456	-0.006
2	5.200	0 0 6	5.188	0.012
3	6.920	0 0 8	6.925	-0.005
4	8.520	$\bar{1}$ $\bar{1}$ 1	8.507	0.013
		and / or		
		1 1 0	8.511	-0.001
5	8.690	0 0 10	8.668	0.021
		and / or		
		0 1 7	8.671	0.019
		and / or		
		1 $\bar{1}$ 2	8.706	-0.016
6	8.950	$\bar{1}$ 1 3	8.961	-0.011
7	9.065	1 1 3	9.042	0.023
8	9.435	1 0 8	9.421	0.014
9	9.535	1 $\bar{1}$ 5	9.554	-0.019
10	9.640	$\bar{1}$ 1 5	9.630	0.010
11	9.790	1 1 5	9.776	0.014
		and / or		
		$\bar{1}$ 0 9	9.789	0.001
12	10.200	$\bar{1}$ $\bar{1}$ 7	10.187	0.013
13	10.440	0 0 12	10.420	0.020
		and / or		
		1 $\bar{1}$ 7	10.453	-0.013
14	10.570	$\bar{1}$ 1 7	10.550	0.020
15	11.855	$\bar{1}$ $\bar{1}$ 10	11.842	0.013
		and / or		
		0 $\bar{2}$ 1	11.856	-0.002
16	12.285	$\bar{1}$ 1 10	12.280	0.005
17	13.975	0 0 16	13.954	0.021
		and / or		
		$\bar{1}$ 2 4	13.970	-0.005
18	17.110	$\bar{1}$ $\bar{2}$ 13	17.128	-0.018
		and / or		
		0 1 18	17.135	-0.025
19	17.370	$\bar{2}$ $\bar{2}$ 4	17.381	-0.011
20	17.510	$\bar{2}$ $\bar{2}$ 3	17.523	-0.013
21	19.350	0 0 22	19.364	-0.014

V as seen in the great resemblance between their diffraction diagrams: only small changes on β and γ angles occur during this phase transition.

III. Spectroscopic Analysis

The spectrum of C10Cu at 294 K shows some splittings of bands at 1492–1480 cm^{-1} (δ_s NH_3), 1472–1467 cm^{-1} (δCH_2), 730–725 cm^{-1}(rCH_2), due to intermolecular coupling between at least two molecules in the unit-cell. The methyl symmetrical deformation, $\delta_s CH_3$, and the ammonium deformations $\delta_a NH_3$ and $\delta_s NH_3$ involve only the vibration of a limited part of the chain. $\delta_s CH_3$ frequency, 1376 cm^{-1}, is similar to that of RT phase of C10Cd: so the interactions between the methyl ends of the cations are nearly the same. $\delta_a NH_3$ and $\delta_s NH_3$ frequencies, 1583 and about 1480 cm^{-1}, respectively, are lower than those in C10Cd spectrum, which suggests that the NH . . . Cl hydrogen bonds are weaker. Well defined progression bands due to intramolecular coupling of adjacent oscillators in an extended chain are observed (Figure 5). They all are accounted for by the presence

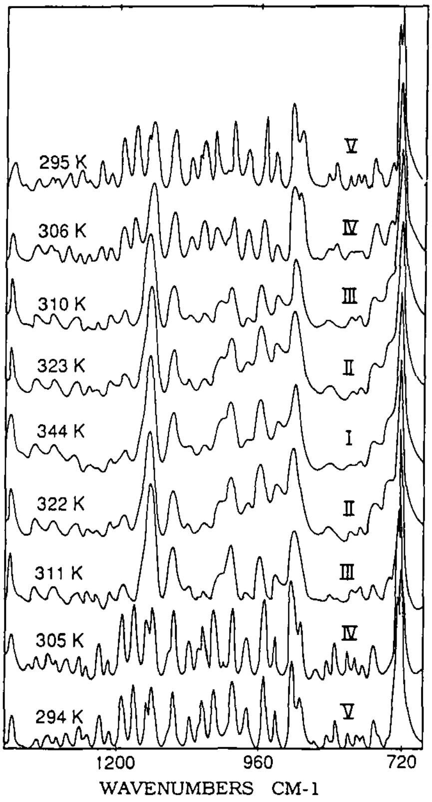


FIGURE 5 Temperature dependence of C10Cu infrared spectrum (in absorbance) between 1400 and 1500 cm^{-1}.

of three conformations, all-trans, A and B.[7] The intrinsic intensity of the rCH_2 vibrations at 810 cm^{-1} (A) and 785 cm^{-1} (B) is the same since integrated intensities of the bands are identical in the RT spectrum of C10Cd.[2] Then integration of the absorbance under the bands at 810 and 785 cm^{-1} of C10Cu shows that the proportion of the B form is 42% of the A form.

Important modifications of the relative intensities are observed when decreasing the temperature; this is most evident in the spectral domain 900–750 cm^{-1} (Figure 6a). Intensities of all-trans vibrations at 796 and 760 cm^{-1} continuously diminish and tend to zero below 100 K. At 100 K, the B type chains are nearly 90% of the A ones and we may admit that there are 50% of A chains and 45% of B chains. To follow the temperature dependence of these intensities, we have chosen the intensity of $\delta_a(NH_3)$ band, at 1585 cm^{-1}, as an internal reference. In that manner, we find that the relative intensity of the 810 cm^{-1} band remains constant when raising temperature while that of the 785 cm^{-1} band continuously decreases; at 292 K there are 50% of A forms and 21% of B forms; consequently the proportion of all-trans conformers progressively increases until 29% (Figure 7). The same results are obtained by considering evolution of the ratio I_{785}/I_{810}. It can be noticed that calculation of the ratios I_{796}/I_{1585} and I_{796}/I_{810} also leads to the above percentages

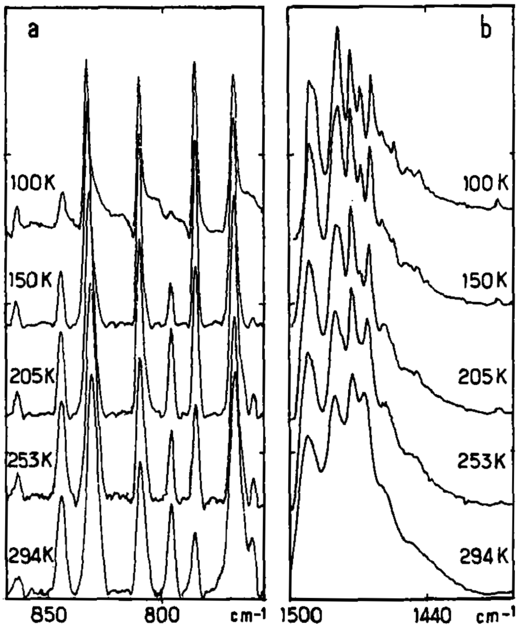


FIGURE 6 Temperature dependence of C10Cu infrared spectrum (in absorbance) below 295 K. a) 680–980 cm^{-1} spectral range; b) 1350–1500 cm^{-1} spectral range.

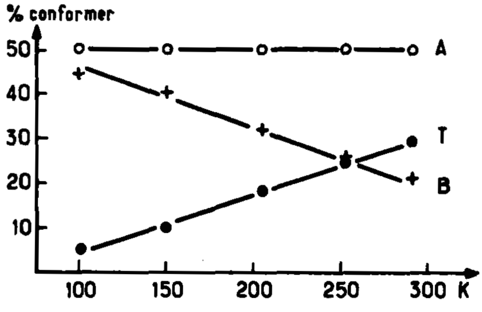


FIGURE 7 Temperature dependence of the proportions of the three conformers of C10Cu (*T* = all-trans chain).

of all-trans forms; this implies that the intrinsic intensity of the rCH_2 vibrations at 796 (all-trans), 810 (A) and 785 cm^{-1} (B) is about the same. Below 205 K, a third component of the δCH_2 splitting is observed at an intermediate frequency (Figure 6b). As chains still consist of t^8, A and B conformers in this temperature range, it is due to the crystalline field effect.

When raising temperature within phase V, for instance at 305 K, the B forms are still 40% of the A ones but the amount of all-trans conformers varies from 58% to 45%. A very weak new broad band simultaneously appears near 1308 cm^{-1}; it is characteristic of kink defects of the form $gt^{2n-1}g^-$ which allow the chains to remain parallel.[2]

In the spectrum of phase IV obtained by cooling at 306 K, the factor group splittings have disappeared; the $\delta_a NH_3$ frequency is shifted from 1583 to 1580 cm^{-1}. This is consistent with a weakening of the intermolecular interactions and of the strength of the hydrogen bonds. The spectrum is typical of extended chains though the peak height of the progression bands is decreased. The kink band at 1308 cm^{-1} and an absorption at 1341 cm^{-1}, assigned to gauche forms in the vicinity of the methyl end, become conspicuous. The spectrum of phase III is characterized by the quasi-disappearance of the progression bands, while the defect bands become the dominant features. The $\delta_a NH_3$ wavenumber decreases further to 1576 cm^{-1} and the $\delta_s CH_3$ frequency is shifted from 1376 to 1378 cm^{-1}, which indicates a decrease in the interactions between the chains layers. The features characteristic of extended chains are no longer observed in the spectrum of phase II. Intensity of the defect bands strongly increases but no new defect such as gg sequences, which should be characterized by an absorption near 1350 cm^{-1}, is detected within the accuracy of our measurements. The spectrum of phase I is strictly identical, above 500 cm^{-1}, to that of phase II. This transition does not seem to imply conformational changes in the chains, which is consistent with the absence of a thermal effect.

DISCUSSION

Five crystalline phases have been evidenced in crystalline $(C_{10}H_{21}NH_3)_2$ $CuCl_4$. Form V belongs to the triclinic system. C10Cu is an ordered solid containing 3 types of extended chains at room temperature. This conclusion is in agreement with X-ray diffraction preliminary results which propose a triclinic cell containing four independent chains: two of type A, one B, and the other one probably T^8, at room temperature.[11] The existence of three bands assigned to a factor group splitting of the δCH_2 mode agrees with the space group P_1 with four molecules in C_1 sites, in the unit cell, below 205 K. When cooling down, a partial conversion of all-trans chains to B chains is evident and at temperature less than 100 K, only the two conformers A and B are present in equal proportions. As the Guinier-Simon diagram does not show any obvious structural modification or phase change when diminishing the temperature until 100 K, evolution of the relative intensity of B and all-trans conformers implies some mobility, at least in the B cavities, within the phase.

The lattice symmetry of form IV is still triclinic but its space group could not be deduced from our powder experiment. It changes to monoclinic (form II) and orthorhombic (form I); the crystallographic system of phase III was not determined. On heating process, V-III and III-II transitions are discontinuous and particularly affect the interlayer distance: the value of d_{002} is equal to 25.2 Å in phase V and to 27 Å in phase III, which corresponds to an increase of 7%. This can be explained by the variation of the tilt angle between the decylammonium cation and the layer. Indeed in phase V, the chains are tilted due to the g bond near the NH_3 end. Infrared measurements show that phase III is highly disordered and that the formation of kinks $gt^{2n-1}g^-$ is important; it is expected that the g^- bond causes the chain end to be parallel to the layer normal. However the interlayer distance in phase III is not sufficient to allow the existence of gtg$^-$ forms; it is consistent with gt^{3}g$^-$ sequences.[7] At the III-II transition a further increase of the interlayer distance, from 27 Å to 27,6 Å, is measured; it can be related to the formation of short kinks gtg$^-$. The athermic II-I transition implies that only the inorganic layers undergo a weak structural modification. By contrast, the IV-V transition which can be observed by cooling involves a thermal effect and does not seem to modify either the crystalline system or the interlayer distance; only the β and γ angles are slightly different. Infrared spectrum analysis shows that a noticeable disorder exists in the hydrocarbon part of phase IV (Figure 5).

It must be noticed that the crystallographic variables abruptly change at the V-III and III-II phase transition temperatures. The chain dynamics evidenced by spectroscopic analysis continuously increase from 100 K up to 330 K with a sharp step at the first transition. The latter is more progressive when decoupled by cooling, since the progression bands reappear in phase IV while the absorption due to specific sequences of bands are still important. However, by contrast with C14Mn[12], coexistence of ordered and disordered clusters is not observed, which suggests that the initiation mechanism of the transition is somewhat different. C10Cu transition behavior also is different from that of C10Cd where the occurrence of interconversion between two types of chain conformers is related to the first transition while a similar phenomenon exists within phase V of C10Cu: this is likely due to the different shape of the chlorine cavities which probably implies a looser packing allowing some mobility of the chains.

Acknowledgments

We warmly thank Dr. K. Schenk of the Université de Lausanne for communicating unpublished results on C10Cu structure. We also thank J. C. Cornut for his valuable technical assistance.

References

1. R. Kind, S. Plesko, H. Arend, R. Blinc, B. Zeks, B. Lozar, J. Slak, A. Levstik, C. Filipic, V. Zagar, G. Lahajnar, F. Milia and G. Chapuis, *J. Chem. Phys.*, **71**, 2118 (1979).
2. L. Ricard, M. Rey-Lafon and C. Biran, *J. Phys. Chem.*, **88**, 5614 (1984).
3. M. R. Ciajolo, P. Corradini and V. Pavone, *Gazz. Chim. Ital.*, **106**, 807 (1976).
4. M. Vacatello and P. Corradini, *Gazz. Chim. Ital.*, **103**, 1027 (1984).
5. M. Kozelj, V. Rutar, I. Zupancic, R. Blinc, H. Arend, R. Kind and G. Chapuis, *J. Chem. Phys.*, **74**, 4123 (1981).
6. F. Barendregt and H. Schenk, *Physica*, **49**, 465 (1970).
7. J. H. Choy, J. K. Kang, J. C. Park, N. B. Chanh and M. Rey-Lafon, *J. Chim. Phys.* (in press).
8. R. Blinc, M. Kozelj, V. Rutar, I. Zupancic, B. Zeks, H. Arend, R. Kind and G. Chapuis, *Far. Disc. Chem. Soc.*, **69**, 58 (1980).
9. M. A. Arriandaga, M. J. Tello, J. Fernandez, H. Arend and J. Roos, *Phys. Stat. Solidii A*, **48**, 53 (1978).
10. K. J. Schenk, *Thesis Lausanne*, (1984).
11. K. J. Schenk, F. J. Zuniga and G. Chapuis, unpublished results.
12. C. Almirante, G. Minoni and G. Zerbi, *J. Phys. Chem.*, **90**, 852 (1986).