

1.02 to 0.93 Å in a temperature range from 130 to 295 K (Doudin & Chapuis, 1988). In the Mn compound, the value of ΔZ at ambient temperature is 1.11 Å (Peterson & Willett, 1972).

The angle ϕ has a sensible influence in the contact region of the methyl end of the chains. Figs. 4(a) and 4(b) show the changes in the geometrical arrangements of the methyl groups. In phase α , the packing is tetragonal; in projection it is nearly hexagonal in phase δ . The tilt angle ϕ corresponds to displacements of the C(3) atoms along \mathbf{a} . The atoms separated by $\Delta y = \frac{1}{2}$ are displaced in opposite directions.

The parameters φ , ϕ and ΔZ are obviously connected to the order parameters of Landau theory applied to these phase transitions, φ and ϕ have the characteristics of order parameters for the $\alpha \rightarrow \beta$ transition, their deviations from zero correspond to the change in the hydrogen-bonding scheme. This effect has been associated with the order parameter used to characterize this transition (Blinic, Žekš & Kind, 1978). The order parameter of the modulated phase γ is directly connected to the modulation of the angle ϕ (Muralt, 1986), and the coupling with strain, used to explain the reentrant character of phase γ , corresponds to a coupling with ΔZ .

Concluding remarks

The study of the three commensurate phases of bis(*n*-propylammonium) tetrachlorocuprate stable above room temperature gives a new insight into the family of compounds with *n*-propylammonium as the organic part. For the first time, complete structural determinations reveal the differences between the two phases β and δ surrounding a modulated phase γ . Our results complete the study of the incommensurate phase γ (Doudin & Chapuis, 1989, 1990). In this family, the specific role played by the copper compound also leads to a more detailed understand-

ing of the microscopic mechanism involved in these phase transitions. In spite of the symmetry differences with respect to the other *n*-propylammonium compounds, the structural changes are characterized by the same geometric arrangements of the organic parts. This strongly supports the central importance of van der Waals interactions between the chains. This work complements the study of Muralt (1986), where the structural arguments justifying the importance of the interactions between chains were limited to comparisons between φ and ϕ .

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Structural Analysis of the High-Temperature Phases of $[\text{NH}_3(\text{C}_3\text{H}_7)_2\text{CuCl}_4]$. II. The Modulated Phase

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Abstract

Between 370 and 435 K, bis(*n*-propylammonium) tetrachlorocuprate shows satellite reflections indicat-

ing a modulated phase. The measurements demonstrate some unusual properties of this phase, specifically the variation of the satellite intensities with temperature. At 400 (2) K, the modulation

vector has a value of $0.175(5)\mathbf{a}^*$ and extinction rules lead to a unique assignment of the superspace group. The refinement reveals a displacive modulation of the layers of CuCl_6 bipyramids with an amplitude along \mathbf{c} (perpendicular to the plane of the layer). Two consecutive layers have displacements opposite in phase. At this temperature the high degree of disorder seriously limits the determination of the modulation of the organic part of the molecule. The reliability of the determination is discussed. The variation of cell parameters and satellite intensities with temperature complete our description of this phase. Crystal data: $M_r = 325.6$, $\text{Cu } K\alpha$, $\lambda = 1.54184 \text{ \AA}$, $\mu = 91.0 \text{ cm}^{-1}$, superspace group $Pbca:(\alpha 00)_{SS0}$, $a = 7.592(3)$, $b = 7.427(2)$, $c = 25.66(1) \text{ \AA}$, $Z = 4$, $wR(F) = 0.090$ for 1076 independent reflections, including 710 first-order satellites.

Introduction

$(\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4$ exhibits four phases α , β , γ and δ above room temperature. The three commensurate phases α , β and δ have been discussed in the preceding article (Doudin & Chapuis, 1990). At nearly 380 K, satellite reflections appear at locations $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$ where $\mathbf{q} \approx 0.18\mathbf{a}^*$ (Holocher, 1986; Jahn, Holocher, Knorr & Ihringer, 1986; Jahn, 1988; Doudin & Chapuis, 1989; Holocher, Jahn, Knorr & Ihringer, 1989). Phase β reenters at the γ - δ transition. Only the analogous compound, where Cu is substituted by Mn (Depmeier, 1981), exhibits the same unusual property. This compound was studied

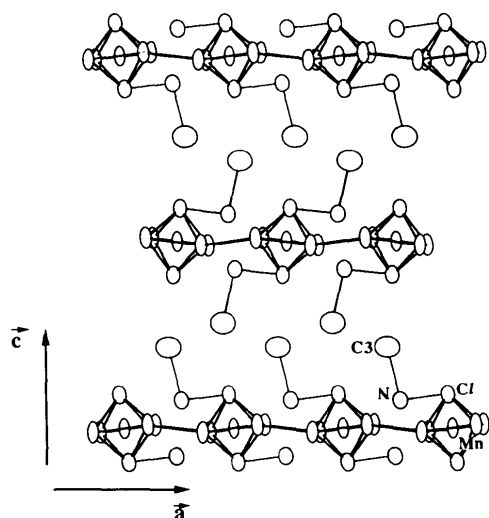


Fig. 1. ORTEP (Johnson, 1965) plot showing a projection along \mathbf{b} of the average structure. The atoms are represented by 50% probability ellipsoids. Cl—Cl connections are shown to illustrate the coordination polyhedron of the Cu atom. Organic chains are represented by the connection between N and C(3).

extensively [see Depmeier (1986) for a review], but no complete structural determination of the γ phase has been performed. This article presents a determination of the modulated structure, which reveals quantitatively the modulations of individual atoms.

The average structure, shown in Fig. 1, is formed by CuCl_6 layers alternating with layers of n -propylammonium chains. The Cu cation induces a Jahn–Teller deformation reflected in the CuCl_6 bipyramids, with four Cl at 2.3 Å from Cu and two Cl at 3.0 Å [see Doudin & Chapuis (1990) and references therein]. The symmetry decreases as compared with the Mn compound, in which the coordination of the Mn atom is nearly octahedral. In spite of this difference, the two compounds have identical vectors of modulation. Our results, including the temperature variation of the cell parameters and the satellite intensities, correspond to the observations made on the Mn compound and confirm the qualitative discussion of Depmeier (1981).

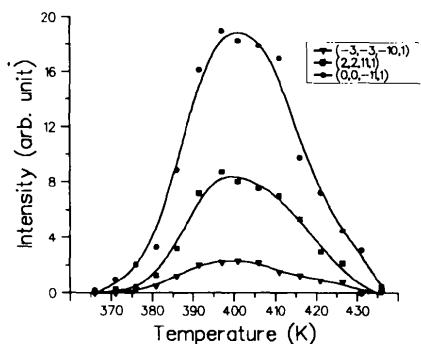


Fig. 2. Variation of the satellite intensity with temperature. The values were obtained by 2θ - ω scans of the reflections. To scale the values with time and thermal decomposition, we postulated that the intensity of the reflection 040 (less affected by the structural differences between phases β and δ) was constant with temperature.

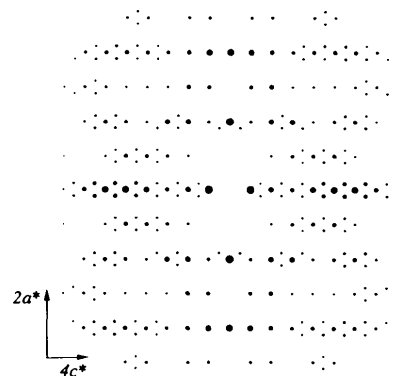


Fig. 3. Representation of the reciprocal hyperplane $h0lm$. The radii of the discs are proportional to $|F_{\text{obs}}|$ (Yamamoto, 1987).

Experimental

The experimental conditions are similar to those reported in Doudin & Chapuis (1990). The temperature was stabilized at 400 K, the temperature at which the satellites show highest intensities (see Fig. 2). The small length of the vector of modulation \mathbf{q} (corresponding to a translation of more than 42 Å, see Fig. 3) calls for the use of Cu radiation to avoid the overlap of the diffraction peaks. The heating device surrounding the crystal reduces the maximum range of 2θ . These two conditions, combined with the thermal decomposition of the sample, limit the number of measurements and the resolution of the data collection.

A sample of dimensions $0.36 \times 0.35 \times 0.015$ mm was used and data were collected on a Syntex R3 diffractometer. Refinements were performed with a local modification of the 'XRAY72 system of programs (Stewart, Kundell & Baldwin, 1972). REMOS85.0 (Yamamoto, 1982) was used to solve the structure by minimizing R^2 , defined as: $R^2 = \sum w(F)(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum w(F)F_{\text{obs}}^2$; $w(F) = 1/\sigma^2(F_{\text{obs}})$ where σ is derived from counting statistics. Atomic scattering factors were taken from Cromer & Mann (1968), and anomalous-dispersion corrections for Cl and Cu atoms were from Cromer & Liberman (1970). Table 1 gives a summary of the data-collection and refinement parameters.*

Symmetry and refinement parameters

The following reflection conditions were observed:

$$\begin{array}{ll} 0, k, l, m & k = 2n \\ h, 0, l, m & l + m = 2n \\ h, k, 0, m & h = 2n. \end{array}$$

Only one satellite reflection with an intensity larger than 3σ was observed in the $h,k,0,m$ reciprocal hyperplane. Fig. 4 shows an ω scan of the $210\bar{1}$ reflection.

With space group $Pbca$ for the average structure (also appearing in phases β and γ), the superspace group can be determined unambiguously as $Pbca:(\alpha 00)ss0$, with the generators: $\{m_x|\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2}\}$, $\{m_y|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0\}$, $\{m_z|\frac{1}{2}, 0, \frac{1}{2}, 0\}$, in addition to the pure translations.

The symmetry operation in $R^4\{m_x|\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2}\}$ fixes the origin of the fourth coordinate \bar{x}_4^u and constrains the inversion center at the origin of R^4 [see Janssen & Janner (1987) for a review and for details of the notation].

* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52336 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Data-collection and refinement parameters

| | | | |
|--|--|-------------|-------|
| Temperature (K) | 400 (2) | | |
| Scan speed ($^\circ \text{ min}^{-1}$) | 1.0 | | |
| Scan width ($^\circ$) | 1.1 (+ 50% for the background) | | |
| Range of hkl | $0 \leq h \leq 5$ $0 \leq k \leq 5$ $-15 \leq l \leq 15$ | | |
| $(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1}) | 0.39 | | |
| Standard reflections | 224, 008, 113 | | |
| Decrease of intensity (%) | 50 | | |
| Transmission factors | $0.23 < T < 0.87$ | | |
| Cell parameters (\AA) | 7.592 (3), 7.427 (2), 25.66 (1) | | |
| a, b, c | | | |
| | $m = 0$ | $m = \pm 1$ | All |
| Non-equivalent reflections | 366 | 710 | 1076 |
| $I \geq 3\sigma$ | 219 | 92 | 311 |
| Weighted R factor (all reflections) | 0.077 | 0.141 | 0.090 |
| Weighted R factor ($I \geq 3\sigma$) | 0.062 | 0.080 | 0.065 |

No higher-order satellites were observed on precession photographs. The measurement of intensities was limited to reflections with their fourth index m equal to $-1, 0, +1$. As a consequence, a sinusoidal form of the modulation expressed by:

$$\begin{aligned} x_i^u(\bar{x}_4^u) = \bar{x}_i^u + U_i^u(\bar{x}_4^u) = \bar{x}_i^u + \text{Re}(U_{1,i}^u)\cos(2\pi\bar{x}_4^u) \\ - \text{Im}(U_{1,i}^u)\sin(2\pi\bar{x}_4^u) \end{aligned}$$

was postulated. \bar{x}_i^u with $i = 1, 2, 3$ is the i th component of the position of the μ th atom in the structure, $U_{n,i}^u$ is the complex amplitude of the n th-order harmonic in the Fourier expansion of the displacement field U_i^u (Yamamoto, 1982).

Only the Cu atom (located at the origin) is on a special position, restricting the value $\text{Re}(U_{1,i}^{\text{Cu}})$ to zero. Unmodulated anisotropic Debye-Waller factors complete the set of parameters used to refine the structure.

Refinement of the structure

Owing to the small number of observed reflections (less than 15% of the satellite reflections show intensities larger than 3σ), the R value was higher than the usual values. The convergence was, however, straightforward and the stability of the solution was good. Table 2 shows the final values refined for all non-H atoms. As in Doudin & Chapuis (1990), the contribution of the H atoms was neglected.

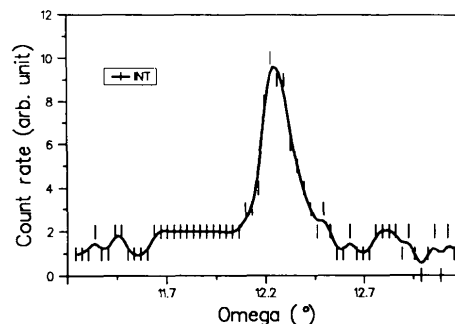


Fig. 4. ω scan of the only satellite reflection ($210\bar{1}$) having an intensity larger than 3σ in the reciprocal hyperplane $hk0m$.

Table 2. Fractional atomic coordinates and modulation parameters

The anisotropic Debye–Waller factors (\AA^2) of the basic and average (refined with main reflections) structures are indicated.

| | | Basic structure | U_0 | $\text{Re}(U_i)$ | $-\text{Im}(U_i)$ |
|-----------------|---|------------------------|--------------|------------------------|------------------------|
| Cu | x | 0.00 | 0.00 | 0.00 | 0.0030 (13) |
| | y | 0.00 | 0.00 | 0.00 | -0.0022 (16) |
| | z | 0.00 | 0.00 | 0.00 | -0.0110 (2) |
| Basic | | $u_{11} = 0.058$ (2) | | $u_{22} = 0.075$ (2) | $u_{22} = 0.153$ (1) |
| | | $u_{12} = -0.010$ (1) | | $u_{13} = 0.006$ (2) | $u_{23} = -0.004$ (2) |
| Average | | $u_{11} = 0.059$ (3) | | $u_{22} = 0.074$ (3) | $u_{33} = 0.187$ (3) |
| | | $u_{12} = -0.010$ (1) | | $u_{13} = 0.002$ (2) | $u_{23} = -0.002$ (4) |
| Cl ₁ | x | 0.2121 | 0.0000 (3) | -0.0035 (17) | 0.0057 (17) |
| | y | 0.2160 | 0.0000 (3) | -0.0035 (18) | -0.0108 (18) |
| | z | -0.0097 | 0.0001 (1) | 0.0009 (6) | -0.0106 (2) |
| Basic | | $u_{11} = 0.064$ (2) | | $u_{22} = 0.065$ (3) | $u_{33} = 0.180$ (3) |
| | | $u_{12} = -0.014$ (2) | | $u_{13} = 0.008$ (3) | $u_{23} = -0.006$ (3) |
| Average | | $u_{11} = 0.066$ (3) | | $u_{22} = 0.068$ (3) | $u_{33} = 0.213$ (3) |
| | | $u_{12} = -0.015$ (2) | | $u_{13} = 0.002$ (2) | $u_{23} = 0.006$ (4) |
| Cl ₂ | x | 0.0381 | -0.0001 (3) | 0.0065 (13) | 0.0046 (16) |
| | y | 0.0073 | 0.0001 (6) | -0.0053 (23) | 0.0095 (23) |
| | z | 0.0886 | 0.0003 (1) | 0.0004 (4) | -0.0107 (2) |
| Basic | | $u_{11} = 0.096$ (2) | | $u_{22} = 0.129$ (4) | $u_{33} = 0.117$ (4) |
| | | $u_{12} = -0.009$ (3) | | $u_{13} = 0.009$ (3) | $u_{23} = 0.001$ (4) |
| Average | | $u_{11} = 0.096$ (4) | | $u_{22} = 0.127$ (5) | $u_{33} = 0.166$ (3) |
| | | $u_{12} = -0.008$ (3) | | $u_{13} = 0.004$ (4) | $u_{23} = -0.009$ (6) |
| N | x | 0.4743 | -0.0008 (14) | 0.0086 (35) | 0.0160 (41) |
| | y | -0.0015 | 0.0000 (20) | -0.0124 (59) | -0.0070 (58) |
| | z | 0.0762 | -0.0016 (4) | 0.0025 (13) | -0.0122 (6) |
| Basic | | $u_{11} = 0.103$ (9) | | $u_{22} = 0.119$ (10) | $u_{33} = 0.050$ (7) |
| | | $u_{12} = 0.016$ (8) | | $u_{13} = 0.024$ (9) | $u_{23} = -0.020$ (14) |
| Average | | $u_{11} = 0.111$ (12) | | $u_{22} = 0.117$ (14) | $u_{33} = 0.120$ (13) |
| | | $u_{12} = 0.007$ (16) | | $u_{13} = 0.000$ (12) | $u_{23} = -0.023$ (20) |
| C(1) | x | 0.5459 | 0.0005 (36) | 0.0137 (84) | 0.0130 (68) |
| | y | 0.0242 | -0.0005 (42) | 0.0021 (122) | 0.0012 (90) |
| | z | 0.1260 | 0.0009 (9) | -0.0001 (26) | -0.0133 (11) |
| Basic | | $u_{11} = 0.249$ (28) | | $u_{22} = 0.232$ (26) | $u_{33} = 0.090$ (26) |
| | | $u_{12} = -0.027$ (23) | | $u_{13} = 0.108$ (20) | $u_{23} = 0.065$ (25) |
| Average | | $u_{11} = 0.266$ (40) | | $u_{22} = 0.258$ (42) | $u_{33} = 0.180$ (43) |
| | | $u_{12} = -0.030$ (16) | | $u_{13} = 0.091$ (12) | $u_{23} = 0.056$ (20) |
| C(2) | x | 0.4871 | -0.0013 (37) | 0.0309 (85) | 0.0130 (78) |
| | y | -0.0277 | -0.0042 (39) | 0.0024 (148) | -0.0112 (100) |
| | z | 0.1667 | 0.0001 (9) | 0.0006 (23) | -0.0145 (13) |
| Basic | | $u_{11} = 0.274$ (34) | | $u_{22} = 0.276$ (33) | $u_{33} = 0.113$ (27) |
| | | $u_{12} = -0.115$ (24) | | $u_{13} = -0.008$ (24) | $u_{23} = -0.040$ (26) |
| Average | | $u_{11} = 0.318$ (49) | | $u_{22} = 0.282$ (49) | $u_{33} = 0.140$ (37) |
| | | $u_{12} = -0.104$ (33) | | $u_{13} = -0.035$ (33) | $u_{23} = -0.038$ (43) |
| C(3) | x | 0.5819 | -0.0002 (32) | 0.0193 (97) | 0.0025 (76) |
| | y | 0.0206 | 0.0008 (34) | 0.0109 (149) | 0.0102 (126) |
| | z | 0.2181 | -0.0007 (8) | 0.0023 (28) | -0.0141 (12) |
| Basic | | $u_{11} = 0.325$ (31) | | $u_{22} = 0.260$ (27) | $u_{33} = 0.216$ (23) |
| | | $u_{12} = -0.070$ (25) | | $u_{13} = -0.056$ (24) | $u_{23} = -0.101$ (27) |
| Average | | $u_{11} = 0.333$ (42) | | $u_{22} = 0.264$ (31) | $u_{33} = 0.273$ (40) |
| | | $u_{12} = -0.063$ (31) | | $u_{13} = -0.050$ (31) | $u_{23} = -0.117$ (33) |

In a sinusoidal approximation, the intensity of the reflection indexed by $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q} = \mathbf{h}_0 + m\mathbf{q}$ is given by:

$$I(\mathbf{H}) \propto \left| \sum_{\mu} f^{\mu}(\mathbf{H}) \exp[2\pi i(\mathbf{h}_0 \cdot \bar{\mathbf{x}}^{\mu})] J_m(2\pi|\mathbf{H} \cdot \mathbf{U}_1^{\mu}|) \right. \\ \left. \times (-1)^m \exp(2\pi i m \phi^{\mu}) \right|^2$$

where J_m is proportional to the spherical Bessel function of order m [see Petriček, Coppens & Becker (1985) and ϕ^{μ} is the argument of $\mathbf{H} \cdot \mathbf{U}_1^{\mu}$: all the phases of the displacements are referred to the origin as is the case in our refinement]. The amplitudes of modulation are mainly in the c direction. If we suppose that the argument in $J_m(2\pi|\mathbf{H} \cdot \mathbf{U}_1^{\mu}|)$ is $\mathbf{U}_1^{\mu} = U_{1,3}^{\mu} \mathbf{c}$, we can directly deduce the absence of measurable satellite reflections in the $hk0m$ hyperplane.

The amplitudes of modulation show values of less than 0.3 \AA , whereas the limit of the resolution of the experiment corresponds to $(\sin \theta / \lambda)_{\text{max}} = 0.4 \text{ \AA}^{-1}$. These two limitations impose a maximal value of nearly 1.5 on the argument $2\pi|\mathbf{H} \cdot \mathbf{U}_1^{\mu}|$ of the Bessel function. With an argument of less than 1.5, J_2 does not contribute to the structure factor. As a consequence, we cannot expect measurable second-order satellite reflections with our limits of resolution.

The small number of observed reflections, the disorder occurring at this temperature and the small atomic scattering factors limit the characterization of the organic part of the structure. It is expressed by the large e.s.d.'s that the structural refinement yields for the corresponding atomic parameters. In the refinement, penalty functions were used to restrict

the interatomic distances of the N and C atoms forming the organic chains. Fig. 5(a) shows that the N—C and C—C distances remain nearly invariant with the phase. The values are similar to those deduced in phases β and δ . An attempt was made to diminish the number of parameters by considering the organic chains as rigid bodies. Linear constraints were imposed between the amplitudes and phases of the N, C(1), C(2) and C(3) atoms; they correspond to rotational and librational modulations of the whole chain about the N atom. The rotations around **a** and **c** were constrained to be unmodulated (see justification in the next paragraph). Table 3 shows a summary of the results. This model cannot be considered as really conclusive: the e.s.d.'s remain large and the *R* factors have appreciably increased.

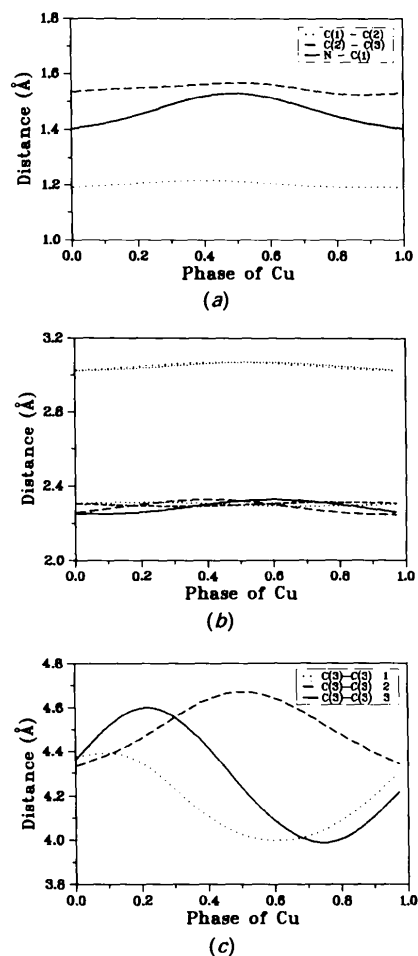


Fig. 5. Interatomic distances modulated with a phase relative to those of the Cu atom located at the origin. The modulation of the atom μ is expressed by: $U^\mu = \frac{1}{2}\{(U_0^\mu + U_1^\mu)\exp 2\pi i[\bar{x}_c^{\text{Cu}} + \mathbf{q} \cdot (\bar{\mathbf{x}}^\mu - \bar{\mathbf{x}}^{\text{Cu}})]\} + \text{c.c.}$ (a) Interatomic distances in the organic chains; (b) interatomic Cu—Cl distances, four curves at ~ 2.3 Å and two at ~ 3.1 Å; (c) interatomic distances separating C(3) atoms of connected chains [the numbers are defined in Fig. 4 of Doudin & Chapuis (1990)].

Table 3. Refined parameters with the organic chain rigid

| Average partial coordinates | | | |
|-----------------------------|----------------------|----------------------|----------------------|
| | <i>x</i> | <i>y</i> | <i>z</i> |
| N | 0.4746 | -0.0005 | 0.0763 |
| C(1) | 0.5504 | -0.0001 | 0.1302 |
| C(2) | 0.4652 | 0.0092 | 0.1687 |
| C(3) | 0.5879 | 0.0040 | 0.2160 |
| Parameters of modulation | | | |
| Component | U_0 | $\text{Re}(U_1)$ | $-\text{Im}(U_1)$ |
| T_x | 0.0016 (12) | 0.0115 (34) | 0.0143 (36) |
| T_y | 0.0020 (18) | -0.0134 (47) | -0.0056 (44) |
| T_z | -0.0004 (4) | 0.0018 (12) | -0.0122 (12) |
| R_x | 0.4 (2) ^a | 2.0 (8) ^a | 0.8 (4) ^a |
| Weighted <i>R</i> factors | | | |
| | $m = 0$ | $m = \pm 1$ | All |
| All reflections | 0.083 | 0.151 | 0.094 |
| $I > 3\sigma$ | 0.067 | 0.091 | 0.070 |

In both models, the inorganic part of the structure remains rigid: the Cu—Cl bond lengths do not vary with the phase of the modulation (Fig. 5b). Fig. 5(c) reveals the variation of the interatomic distances separating the ends of the organic chains [also discussed in Doudin & Chapuis (1990)].

Discussion

The modulated structure of phase γ is mainly characterized by atomic displacements with amplitudes along **c**. Two successive CuCl_4 layers have a phase difference of π induced by the symmetry element $\{m_y | 0, \frac{1}{2}, \frac{1}{2}\}$. All the atoms are nearly in phase, with the same amplitude along **c** (see Table 4). For the organic part, the amplitudes are slightly larger. The contribution of the modulated rotation around **b** has also been taken into account in Fig. 6. This diagram illustrates the modulation and is directly inspired by the study of the Mn compound (Muralt, 1986; Muralt, Caravatti, Kind & Roos, 1986).

The refinement with a rigid organic chain was also performed with the intention of comparing our results with those deduced by quadrupole-perturbed NMR measurements for the Mn compound (Muralt *et al.*, 1986). In this experiment, the angle ζ [angle of rotation of the N—C(1) bond around **b**] is modulated with an amplitude reaching a maximum of 4° . In the Cu compound, this bond does not show any sensible modulated rotation with the first refinement model. With the rigid-body model, this value was determined as $2.2(1.0)^\circ$. As discussed earlier, our X-ray experiments, despite their uncertainty, are compatible with those obtained by Muralt *et al.* (1986).

Fig. 7 also gives a physical and intuitive confirmation of the parameters characterizing the organic part of molecule. It shows the distance between adjacent chains and the distance separating connected ends of chains along **c** [this corresponds to

Table 4. Amplitudes and phases of the modulation along *c*

| | Amplitude (Å) | Phase (°) | $t = 360q(\bar{x}^u - \bar{x}^{Cu})$ (°) |
|------------------------------|---------------|-----------|--|
| Cu | 0.282 (5) | 0 | 0 (by definition) |
| Cl ₁ | 0.273 (6) | 5 (3) | 14 |
| Cl ₂ | 0.275 (6) | 2 (2) | 2.5 |
| N | 0.32 (3) | 12 (6) | 30 |
| C(1) | 0.31 (4) | 0 (13) | 36 |
| C(2) | 0.37 (4) | 0 (13) | 32 |
| C(3) | 0.37 (4) | 9 (11) | 38 |
| T ₁ (rigid model) | 0.32 (4) | 9 (6) | 30 |

ΔZ defined in Doudin & Chapuis (1990)] with modulations out of phase by approximately $\pi/2$. In other words, the space for a methyl end of an 'up' chain is maximal (adjacent 'down' chains have a maximal distance of separation) when the intralayer distance is minimal.

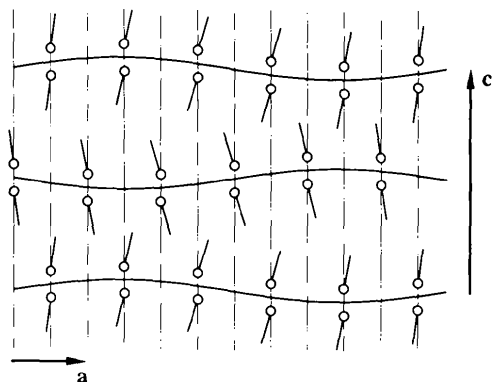


Fig. 6. Diagram reproducing the shape of the modulation in a projection along *b*. Modulated planes at $z = 0, \frac{1}{2}, 1$, corresponding to the CuCl_4 layers, are shown. The circles represent the ammonium end of the organic chains and the lines the propyl part of the chains. The amplitudes of modulation are doubled for the illustration.

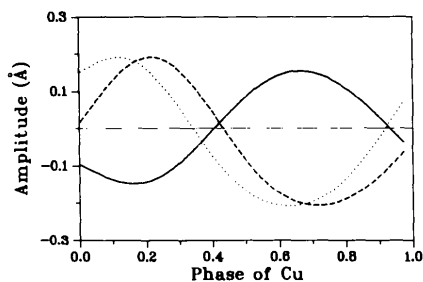


Fig. 7. Modulation of the distance along *c* separating C(3) atoms of interconnected chains. For any atom C(3) 'up' ($z > 0.25$), two phases of the C(3) end of 'down' chains ($z < 0.25$) are found (dotted and dashed lines). For symmetry reasons, these two functions are essentially determined by the amplitudes of modulation along *c*. The third function (full line) represents the modulation of the distance separating two adjacent chains (separated by a translation along *a*), and corresponds to the two 'down' chains.

 Table 5. Values of the parameters ϕ , φ and ΔZ [defined in Doudin & Chapuis (1990)] for the average structure

| Values for phases β and δ are given for comparison. | | | |
|--|------------|---------------|----------------|
| | ϕ (°) | φ (°) | ΔZ (Å) |
| Phase β | 5.4 (1) | 11.7 (9) | 2.03 (8) |
| Phase γ (average) | 7.2 (2) | 12.6 (1.3) | 1.64 (4) |
| Phase δ | 8.4 (1) | 15.8 (4) | 1.02 (2) |

To compare the average structure with those of the β and δ phases, we used the parameters φ , ϕ and ΔZ , as defined in Doudin & Chapuis (1990). Phase γ can be characterized by means of their modulation (Fig. 6 was derived from the modulations of φ and ΔZ). If we suppose a rigid chain, φ is equal to ζ . Not surprisingly, we find intermediate values for φ , ϕ and ΔZ in comparison with those obtained in phases β and δ (Table 5). Fig. 8 shows the variation of ΔZ in phase γ . The parameter ΔZ , modulated with an amplitude twice the calculated atomic amplitudes along *c* (Table 4), expresses the tendency to reach the values corresponding to the phases δ and β ; they are approximately 1 and 2 Å respectively. Near the temperature of transition from $\gamma \rightarrow \delta$ or $\gamma \rightarrow \beta$, the amplitude of ΔZ diminishes, thus avoiding exceeding the limits of ΔZ observed in phases δ and β (represented by the arrows in Fig. 8). The variation of satellite intensities with temperature is directly related to the variation of this amplitude. It is more difficult to detect a corresponding behaviour of ϕ and φ ; their variations are smaller and the determination of their amplitudes by X-ray diffraction is not straightforward.

Fig. 9 shows the variations of the cell parameters with temperature. This also corresponds to the measurements of the thermal expansion characterizing the Mn compound (Murali, 1986). Note that $|\mathbf{a} \times \mathbf{b}|$ is nearly invariant in a temperature range of more than 200 K. This expresses the rigidity of the

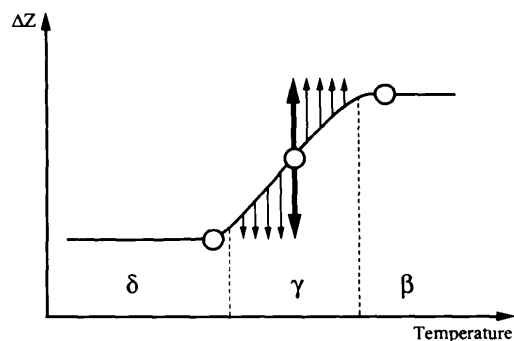


Fig. 8. Scheme representing the variation of the structural parameter ΔZ [defined in Doudin & Chapuis (1990)] with temperature. Circles indicate the values determined in phases β , γ and δ . The bold arrows correspond to the modulation amplitude of ΔZ .

CuCl_6 bipyramids. As a consequence, the volume variation is similar to the variation of the cell parameter c .

Concluding remarks

The modulated phase γ of bis(n -propylammonium) tetrachlorocuprate has a reentrant character shown by the unusual variation of the intensities of satellite reflections. The structural determination reveals the amplitudes of modulation along c , perpendicular to the inorganic layers. Atoms in successive layers have opposite displacements. As a consequence, the distance separating the methyl ends of the organic

chains along c is modulated with a large amplitude reaching 0.6 Å. Changing from phase δ to phase γ , the compound adopts a modulated phase in order to optimize the van der Waals packing of the chains by reducing this vertical distance from 2 to 1 Å. In spite of the differences in the geometry of the inorganic part, this compound shows strong analogies with the Mn derivative. This structural determination also completes the model of the Mn compound.

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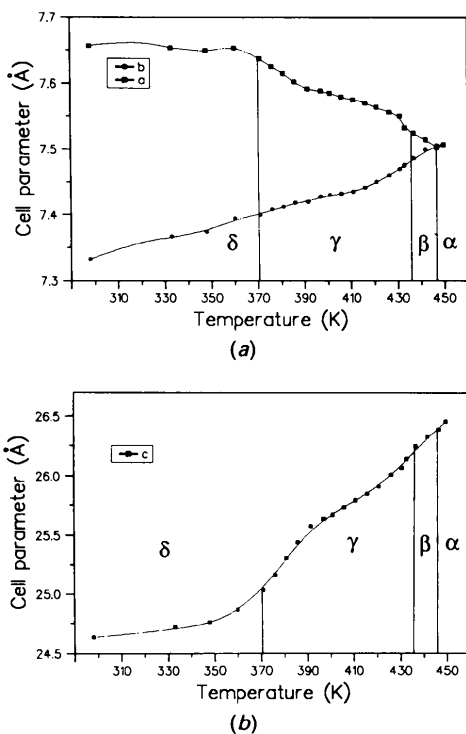


Fig. 9. (a), (b) Variation with temperature of the cell parameters. The e.s.d.'s are smaller than the plotted data.

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