

Structure Analysis of the High-Temperature Phases of $[\text{NH}_3(\text{C}_3\text{H}_7)]_2\text{CuCl}_4$. I. The Commensurate Phases

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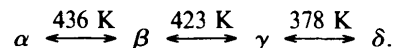
Abstract

Bis(*n*-propylammonium) tetrachlorocuprate shows four phases (α , β , γ , δ) above room temperature. The determination of the three phases α , β and δ by single-crystal diffraction is discussed. The structures are formed by CuCl_4 layers parallel to the *ab* plane alternating with layers of organic chains. Phases β and δ have the same space group, *Pbca*, which points to the unusual character of the modulated phase γ . Phase α , which occurs at the highest temperature, is also orthorhombic (*Bbcm*), but with $a = b$. The main structural differences between the three phases can be expressed in terms of three quantities: the distance along *c* separating the organic chains, and the tilt angles of the CuCl_6 bipyramids and of the organic chains around *b*. The Jahn–Teller deformation of the CuCl_6 bipyramids reduces the symmetry as compared with other *n*-propylammonium compounds. However, the neighbourhood of the organic part of the molecule is analogous, indicating the leading role played by the *n*-propylammonium group in these phase transitions. Crystal data: $M_r = 325.6$, $\mu = 24.6 \text{ cm}^{-1}$, $\text{Mo K}\alpha$, $\lambda = 0.71069 \text{ \AA}$. Phase α (450 K): space group *Bbcm*, $a = 7.506$ (6), $b = 7.506$ (5), $c = 26.45$ (2) \AA , $V = 1490$ (4) \AA^3 , $Z = 4$, $wR(F) = 0.050$ for 173 independent reflections. Phase β (433 K): space group *Pbca*, $a = 7.530$ (5), $b = 7.474$ (4), $c = 26.14$ (2) \AA , $V = 1471$ (3) \AA^3 , $Z = 4$, $wR(F) = 0.044$ for 329 independent reflections. Phase δ (360 K): space group *Pbca*, $a = 7.653$ (3), $b = 7.394$ (3), $c = 24.86$ (2) \AA , $V = 1407$ (3) \AA^3 , $Z = 4$, $wR(F) = 0.054$ for 687 independent reflections.

Introduction

Within the family $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MX}_4$, the compound $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4$ plays a particular role for at least two reasons. Firstly, the presence of copper induces a Jahn–Teller deformation of the MX_6 octahedra (Jahn, Knorr & Ihringer, 1989): the copper cation has (4 + 2) coordination with four Cl neighbours at nearly 2.3 \AA and two Cl located in the *ab* plane at nearly 3.0 \AA . The polyhedron is rather a bipyramid with the bases approximately perpendicular to the *ab* plane. Secondly, the *n*-propylammonium ion favours the appearance of modulated

phases, as observed for $M = \text{Cd}$ (Doudin & Chapuis, 1988) or Mn (Depmeier & Mason, 1983). At high temperature, a modulated phase has also been observed for the Cu derivative (Holoher, 1986; Jahn, Holoher, Knorr & Ihringer, 1986; Jahn, 1988; Doudin & Chapuis, 1989, 1990; Holoher, Jahn, Knorr & Ihringer, 1989). The temperatures of the phase transitions have been determined by optical methods (Etxebarria, Ruiz-Larrea, Tello & López-Echarri, 1988). The phase sequence is:



Phase β has a reentrant character since phase δ has the same space group. The purpose of this article is to present a complete structural determination of phases α , β and δ . The aim is to show the structural differences between β and δ , and to compare the β – α transition with the usual tetragonal-to-orthorhombic transition occurring in members of this series unaffected by Jahn–Teller deformation. The structure of phase δ has already been determined at room temperature (Barendregt & Schenk, 1970). However, a new measurement near the temperature of occurrence of phase δ has been obtained. A comparison of the results should provide some useful information.

The structure is characterized by inorganic layers of CuCl_6 bipyramids forming a chessboard-like configuration parallel to the *ab* plane (Fig. 1). In the cavities, the ammonium ends of the *n*-propylammonium chains are connected by hydrogen bonds. Chains connected to the same inorganic layer and having the same direction (approximately parallel to *c*) are called 'adjacent'. The set of adjacent chains composed of atoms with fractional coordinate *z* less than 0.25 will be called 'down' chains. The other set of adjacent chains with *z* between 0.25 and 0.5, will be called 'up' chains. Up and down chains are connected by van der Waals interactions of their methyl ends (Fig. 2).

Experimental

Single crystals were grown on the surface of an aqueous solution and mounted directly on a glass fibre. The samples were protected with silicon grease

to limit the effect of thermal decomposition. The sample was heated by means of a U-shaped rod enveloping the crystal. The whole assembly was wrapped with a thin Mylar sheet in order to improve the temperature stability within a range of less than 1 K. A Cu/Ni thermocouple was used to monitor the temperature. The temperatures of measurement were 360, 433 and 450 K for phases δ , β and α , respectively. Phase δ was measured by increasing the temperature a few K before the appearance of satellite intensities of phase γ . The disappearance of the satellite reflections was assumed to indicate the existence of phase β ; at higher temperature, the changes in the diffraction pattern indicated the transition to phase α .

X-ray diffraction intensities were collected on a Syntex R3 diffractometer. A sample with dimensions $0.2 \times 0.2 \times 0.02$ mm was used for phase δ , whereas a larger sample of $0.7 \times 0.4 \times 0.05$ mm was used for phases β and α .

The structures were solved with the aid of the XRAY72 system of programs. (Stewart, Kundell &

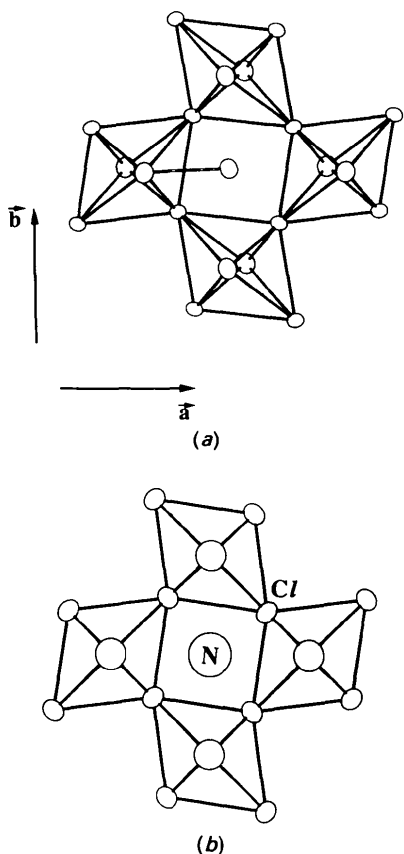


Fig. 1. ORTEP (Johnson, 1965) plots showing projections of the structure along c . Only one N and the Cl atoms are indicated. (a) Phase δ , (b) phase α . Note the tetragonal environment of the N atom.

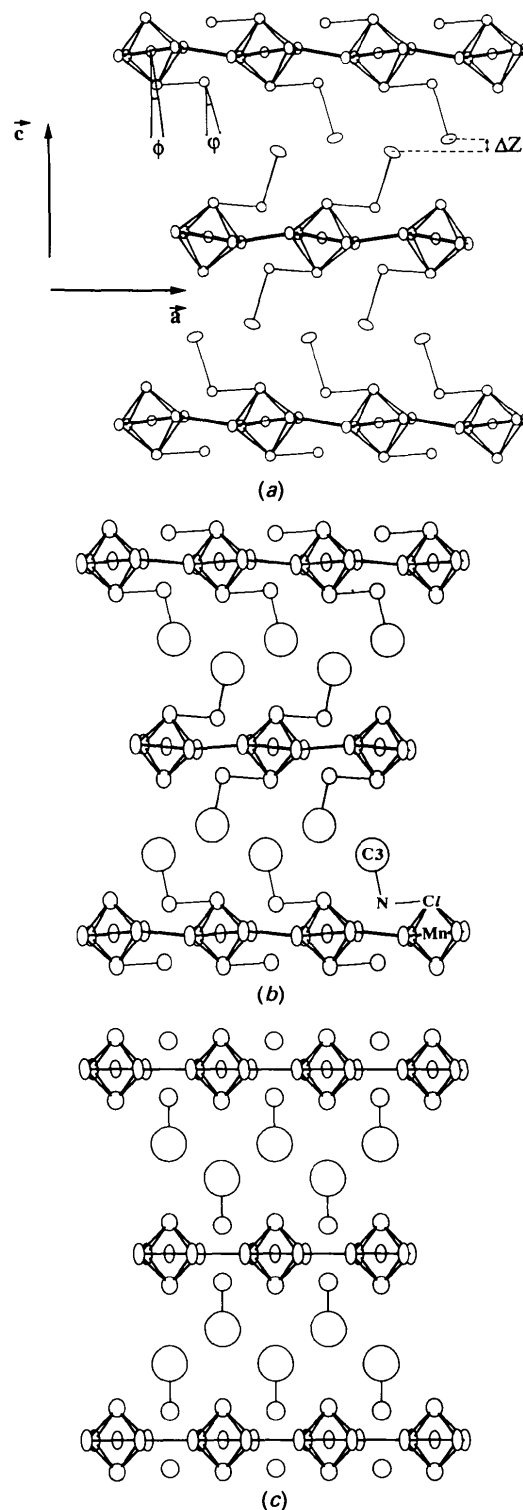


Fig. 2. ORTEP (Johnson, 1965) plots showing projections of the structures along b : 50% ellipsoids are indicated. The organic chains are represented by the N and the last C(3) atoms. In phases δ and β the hydrogen-bonding scheme corresponding to the frozen rotations around b is indicated. (a) Phase δ , (b) phase β , (c) phase α .

Table 1. *Data-collection and refinement parameters*

Phase	δ	β	α
Temperature (K)	360 (1)	433 (1)	450 (1)
Scan speed ($^{\circ}$ min $^{-1}$)	1.0-4.2	5.6-14.7	5.6-14.7
Scan width ($^{\circ}$)	1.2	1.2	1.2
(+ 50% for the background)			
Range of hkl	$0 \leq h \leq 7$ $-7 \leq k \leq 7$ $0 \leq l \leq 26$	$-6 \leq h \leq 6$ $-6 \leq k \leq 6$ $-22 \leq l \leq 22$	$-6 \leq h \leq 0$ $-6 \leq k \leq 6$ $-22 \leq l \leq 22$
$(\sin \theta / \lambda)_{\max}$ (\AA^{-1})	0.54	0.42	0.42
Standard reflections	3,0,10 442 0,0,10	0,4,10 2,2,10 0,0,10	0,4,10 311 0,0,10
Decrease of intensity (%)	20	50	70
Transmission factors			
Minimum	0.42	0.27	0.27
Maximum	0.93	0.70	0.70
Cell parameters (\AA)			
<i>a</i>	7.653 (3)	7.530 (5)	7.506 (6)
<i>b</i>	7.394 (3)	7.474 (4)	7.506 (5)
<i>c</i>	24.86 (2)	26.14 (2)	26.45 (2)
Non-equivalent reflections	919	468	463
$I \geq 3\sigma$	687	329	173
Number of variables	61	46	25
Internal <i>R</i> factor	0.047	0.067	0.076
<i>R</i> factor	0.049	0.048	0.044
Weighted <i>R</i> factor	0.054	0.044	0.050
Goodness of fit	3.53	3.24	1.87
Highest peak found on final difference Fourier map ($e \text{\AA}^{-3}$)	0.6	0.4	0.3

Baldwin, 1972). *R* factors resulting from a full-matrix least-squares refinement were defined as: $R = [\sum w(F)(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum w(F)F_{\text{obs}}^2]^{1/2}$; $w(F) = 1/\sigma^2(F_{\text{obs}})$, where σ is derived from counting statistics, averaging and scaling of the intensities with time.

The applied linear absorption coefficient μ was 24.76 cm^{-1} . Atomic scattering factors were taken from Cromer & Mann (1968); the anomalous-dispersion correction for Cl and Cu atoms was applied with values calculated by Cromer & Liberman (1970). Table 1 gives a summary of the data-collection parameters. The decrease of the intensities with time was larger with increasing temperature. A frequent and rapid measurement of standard reflections indicated, however, a convincing linear scaling of the measurements with time.*

Structure of phase δ

The space group of phase δ , measured at 360 (1) K, is *Pbca*; it was directly deduced from extinction rules and confirmed the results of Barendregt & Schenk (1970) and Jahn *et al.* (1986). The cell parameters were obtained by centring 16 reflections with 2θ from 22 to 28°. In the course of the measurement, their values remained constant within their e.s.d.'s.

The refinement was performed without H atoms. For the three phases, the disorder of the organic part is so important that taking into account the hydro-

gen contribution in the model would be meaningless.

The positions of the C atoms must be considered as average values. The small C—C distances are characteristic of disordered organic chains. The ammonium end is linked by hydrogen bonds to two axial Cl atoms (*i.e.* out of the *ab* plane) and one equatorial Cl atom (*i.e.* nearly in the *ab* plane). The chains and the CuCl_6 bipyramids show a tilt angle around *b* (Fig. 2*a*). As a consequence, one axial Cl atom has a privileged bonding distance [the connection is indicated in Figs. 1(*a*), 2(*a*) and 2(*b*)]. If the symmetry is not reduced by Jahn–Teller deformation, the connection of the ammonium end is similar: in the Cd and Mn compounds, the symmetry of the room-temperature phases restricts the average position of the chains to $y = 0$ or $\frac{1}{2}$. With this symmetry, two possible hydrogen-bonding schemes can be deduced for the ammonium end. In the copper compound, this symmetry restriction vanishes, but the atomic arrangement ($y \approx 0$ in Table 2) also corresponds to the same types of bonding schemes.

The results are in agreement with those obtained by Barendregt & Schenk (1970); Table 2 gives a summary of their coordinates. At room temperature, the cell parameters are nearly identical. The disorder was, however, approximated by splitting the C(2) and C(3) atoms. Similar attempts with our measurements did not improve the refinement.

Structure of phase β

At 433 (3) K the satellite reflections vanish [Etzbarria *et al.* (1988) found a lower transition temperature of 423 K] and the space group is again *Pbca*. However, the cell parameter *c* has increased, providing additional space for the organic chains. The positions of the C atoms were refined with isotropic Debye–Waller factors and the C—C distances were restrained to the values determined in phase δ . Attempts to refine the whole chain with anisotropic Debye–Waller factors increased the goodness-of-fit without improving the *R* factors. The final parameters are indicated in Table 3. Figs. 3(*a*), 3(*b*) and 3(*c*) show the disappearance of the electron density corresponding to the C atoms. It is caused by the very large disorder exhibited at this temperature.

Structure of phase α

The transition was observed at approximately 445 K and the measurements were performed at 450 (1) K. The space group is *Bbcm* with *a* equal to *b* within their e.s.d.'s [in agreement with Jahn *et al.* (1986, 1989)]. The symmetry of the diffraction pattern clearly excludes tetragonal symmetry indicating a persistence of the Jahn–Teller deformation. All the atoms are on special positions and the organic chains

* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52334 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates and anisotropic Debye–Waller factors of phase δ

Diagonal elements U_{ii} are given in $\text{\AA}^2 \times 10^2$. The results of Barendregt & Schenk (1970) are shown in italic. U indicates isotropic Debye–Waller factors ($\text{\AA}^2 \times 10^2$).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>	U_{11}	U_{22}	U_{33}
Cu	0.00 <i>0.00</i>	0.00 <i>0.00</i>	0.00 <i>0.00</i>		3.7 (1) <i>2.9</i>	4.0 (1) <i>3.1</i>	8.2 (1) <i>4.7</i>
Cl _v	0.2118 (2) <i>0.2114</i>	0.2170 (2) <i>0.2177</i>	-0.0114 (1) <i>-0.0123</i>		4.3 (1) <i>1.6</i>	4.1 (1) <i>1.0</i>	10.8 (2) <i>5.5</i>
Cl _a	0.437 (2) <i>0.0462</i>	0.0099 (3) <i>0.0117</i>	0.0910 (1) <i>0.0917</i>		5.5 (1) <i>2.8</i>	8.4 (1) <i>3.8</i>	7.8 (1) <i>3.8</i>
N	0.4684 (8) <i>0.4679</i>	-0.0017 (9) <i>-0.0021</i>	0.0811 (3) <i>0.0825</i>	3.7	6.4 (4) <i>6.4 (4)</i>	8.0 (4) <i>8.0 (4)</i>	6.5 (4) <i>6.5 (4)</i>
C(1)	0.5493 (25) <i>0.5410</i>	0.0088 (24) <i>0.0063</i>	0.1314 (6) <i>0.1273</i>	8.9	21 (2) <i>38 (4)</i>	20 (1) <i>38 (3)</i>	9.2 (9) <i>11 (1)</i>
C(2)	0.5186 (37) •	0.0042 (40) •	0.1740 (7) <i>0.1789</i>	•	38 (4) <i>19 (1)</i>	38 (3) <i>21(1)</i>	11 (1) <i>8.8 (8)</i>
C(3)	0.6049 (20) •	0.0136 (17) •	0.2294 (5) <i>0.2353</i>	•	19 (1) <i>19 (1)</i>	21(1) <i>21(1)</i>	8.8 (8) <i>8.8 (8)</i>

* For split atoms only the *z* coordinate is indicated.

Table 3. Fractional atomic coordinates and Debye–Waller factors ($\text{\AA}^2 \times 10^2$) of phase β

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>	U_{11}	U_{22}	U_{33}
Cu	0.00	0.00	0.00		5.7 (1)	5.4 (1)	16.6 (2)
Cl _v	0.2142 (3)	0.2151 (3)	-0.0068 (1)		6.3 (2)	5.9 (2)	20.7 (4)
Cl _a	0.0287 (6)	0.0084 (7)	0.0869 (1)		10.7 (3)	12.3 (3)	16.3 (4)
N	0.4770 (19)	-0.0013 (19)	0.0776 (5)		11.1 (8)	11.6 (6)	13 (1)
C(1)	0.5449 (37)	0.0049 (36)	0.1293 (12)	26 (1)			
C(2)	0.4748 (73)	0.0192 (75)	0.1669 (17)	49 (4)			
C(3)	0.5727 (49)	0.0076 (62)	0.2111 (16)	45 (3)			

Table 4. Fractional atomic coordinates and Debye–Waller factors ($\text{\AA}^2 \times 10^2$) of phase α

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>	U_{11}	U_{22}	U_{33}
Cu	0.00	0.00	0.00		5.8 (2)	6.4 (2)	16.3 (4)
Cl _v	0.2147 (3)	0.2152 (5)	0.00		6.3 (2)	6.7 (4)	23.0 (8)
Cl _a	0.00	0.00	0.0857 (3)		13.8 (3)	13.7 (5)	16.6 (8)
N	0.50	0.00	0.0764 (8)	13.7 (5)			
C(1)	0.50	0.00	0.1240 (28)	32 (3)			
C(2)	0.50	0.00	0.1573 (34)	41 (7)			
C(3)	0.50	0.00	0.2052 (33)	53 (4)			

are constrained to lie on a twofold axis. Very soft restraints were applied to the interatomic distances of the organic part of the molecule to avoid divergence of the refinement. The results are given in Table 4.

The nearly tetragonal neighbourhood of the chains can be observed in Fig. 1(b). As a consequence, four geometrically equivalent possible connections of the ammonium head exist. Here again, the Jahn–Teller deformation only decreased the symmetry, without affecting the atomic arrangement of the organic part. The C—C distances described in Table 5 must be considered as average values separating the atoms; they can be compared with the distances calculated for phases δ and β if their projected lengths on *c* are evaluated:

$$\text{Phase } \delta: \quad [\text{N—C(1)}]_z = 1.25 \text{ \AA} \quad [\text{C(1)—C(2)}]_z = 1.06 \text{ \AA} \\ [\text{C(2)—C(3)}]_z = 1.38 \text{ \AA}$$

$$\text{Phase } \beta: \quad [\text{N—C(1)}]_z = 1.35 \text{ \AA} \quad [\text{C(1)—C(2)}]_z = 0.98 \text{ \AA} \\ [\text{C(2)—C(3)}]_z = 1.16 \text{ \AA}$$

Discussion

Let us first introduce three quantities describing the structural differences between the three phases. The quantities are as follows:

(a) The tilt angle φ of the organic chains, which defines the rotation angle of the N—C(3) axis around **b**. As the chains are mainly parallel to the *ac* plane, φ is the angle between the *c* and the N—C(3) directions (see Fig. 2a).

(b) The tilt angle ϕ of the inorganic bipyramids, which defines the rotation angle of the Cu—Cl_a direction around **b** (see Fig. 2a).

(c) The 'interchain' parameter ΔZ , which corresponds to the projection along *c* of the distance separating two C(3) atoms of interconnected chains (also shown in Fig. 2a).

Table 6 lists the values of φ , ϕ and ΔZ for the three phases. In phase α , φ and ϕ are constrained by symmetry to zero (chains perpendicular to the *ab* plane). The value of ΔZ is correlated to the cell

parameter c , but the variations in the fractional coordinate z of the atom C(3) with temperature (connected to the variation of φ) also contribute to the changes in ΔZ .

In the temperature interval of phase δ , the values of the parameters defined above do not show a large variation. Barendregt & Schenk (1970) reported a shorter value of ΔZ for the structure at ambient temperature. However, their model of split atoms

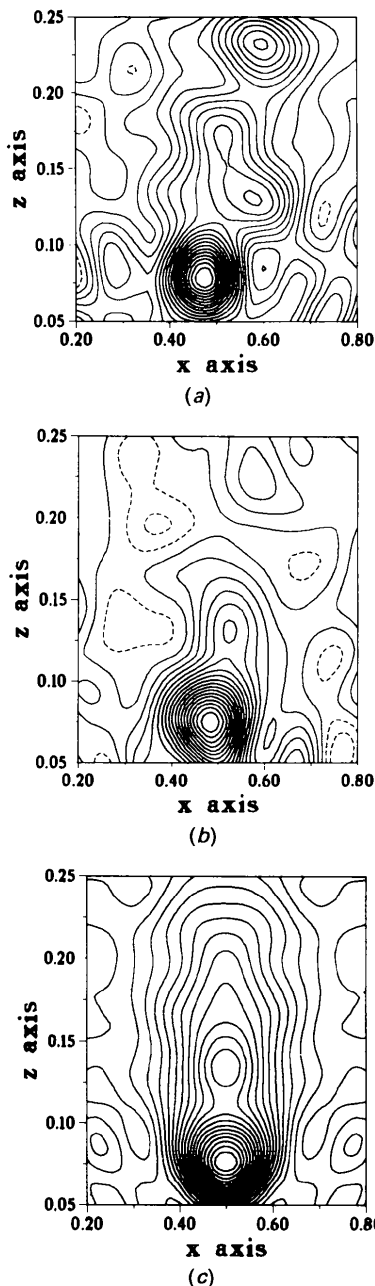


Fig. 3. The Fourier summations showing the electronic density of the organic chains. The function is integrated along b within the limits $-0.15 \leq y \leq 0.15$. (a) Phase δ , (b) phase β , (c) phase α .

Table 5. *Interatomic distances* (\AA) *for the three phases*

Cl_i denotes the Cl_i atom indicated in Tables 2–4 and transformed by the symmetry element $\{2, \frac{1}{2}, \frac{1}{2}, 0\}$. Cl_i' is the atom Cl_i translated by $+a$. The connections expressed by numbers correspond to Fig. 4.

Atoms connected	δ	β	α
Cu— Cl_i'	3.053 (2)	3.033 (2)	3.026 (3)
Cu— Cl_i	2.288 (2)	2.284 (2)	2.267 (7)
N— Cl_i	3.261 (6)	3.39 (1)	3.762 (2)
N— Cl_i'	4.410 (6)	4.16 (1)	3.762 (2)
N— Cl_i	3.30–3.43	3.35–3.38	3.348–3.353
N—C(1)	1.40 (2)	1.44 (2)	1.26 (3)
C(1)—C(2)	1.09 (2)	1.12 (5)	0.89 (6)
C(2)—C(3)	1.53 (2)	1.37 (5)	1.26 (4)
1	3.96 (2)	4.28 (4)	4.44 (4)
2	4.31 (2)	4.59 (4)	5.31 (4)
3	4.16 (2)	4.39 (4)	4.44 (4)

Table 6. *Values of the parameters* ϕ , φ *and* ΔZ *(defined in the text) for the three phases*

	δ	β	α
φ ($^\circ$)	15.8 (4)	11.7 (9)	0
ϕ ($^\circ$)	8.4 (1)	5.4 (1)	0
ΔZ (\AA)	1.02 (2)	2.03 (8)	2.37 (17)

with isotropic Debye–Waller factors cannot be directly compared with the values reported here. At approximately 220 K, still in phase δ , a value of ΔZ of 0.95 \AA was deduced from an additional set of measurements. In the Cd compound, ΔZ varies from

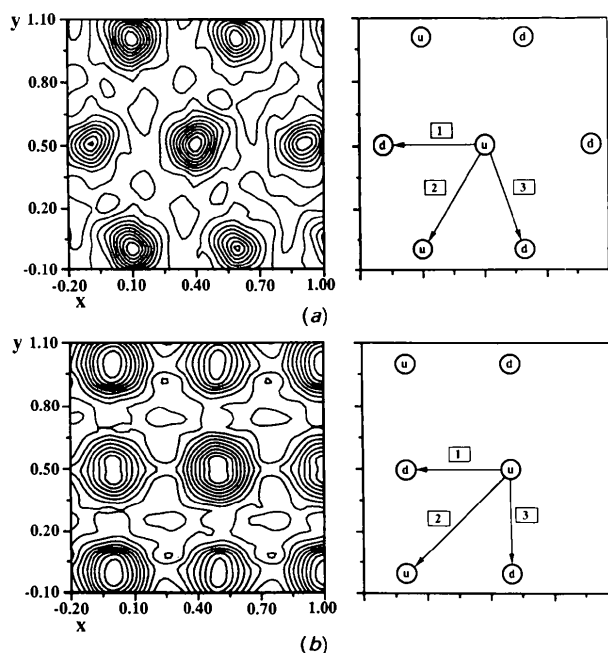


Fig. 4. The Fourier summations showing the electronic density of the methyl end groups. This function is integrated along c within the limits $-0.22 \leq z \leq 0.30$. The atomic positions and distances calculated in Table 5 are also indicated by the schemes. 'u' and 'd' denote 'up' and 'down' organic chains, respectively. The numbers correspond to the interatomic distances given in Table 5. (a) Phase δ , (b) phase α .

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 **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 .

References

- BARENDREGT, F. & SCHENK, H. (1970). *Physica*, **49**, 465–468.
 BLINC, R., ŽEKŠ, B. & KIND, R. (1978). *Phys. Rev. B*, **17**, 3409–3420.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 DEPMEIER, W. & MASON, S. A. (1983). *Solid State Commun.* **46**, 409–412.
 DOUDIN, B. & CHAPUIS, G. (1988). *Acta Cryst.* **B44**, 495–502.
 DOUDIN, B. & CHAPUIS, G. (1989). *Phase Transitions*, **16/17**, 185–190.
 DOUDIN, B. & CHAPUIS, G. (1990). *Acta Cryst.* **B46**, 180–186.
 ETXEBARRIA, J., RUIZ-LARREA, I., TELLO, M. J. & LÓPEZ-ECHARRI, A. (1988). *J. Phys. C*, **21**, 1717–1725.
 HOLOCHER, K. (1986). Dipl. Thesis, Univ. Tübingen, Federal Republic of Germany.
 HOLOCHER, K., JAHN, I. R., KNORR, K. & IHRINGER, J. (1989). In preparation.
 JAHN, I. R. (1988). Private communication.
 JAHN, I. R., HOLOCHER, K., KNORR, K. & IHRINGER, J. (1986). *Z. Kristallogr.* **174**, 102–103.
 JAHN, I. R., KNORR, K. & IHRINGER, J. (1989). *J. Phys. Condens. Matter*. In the press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 MURALT, P. (1986). *J. Phys. C*, **19**, 1689–1704.
 PETERSON, E. R. & WILLET, R. D. (1972). *J. Chem. Phys.* **56**, 1879–1882.
 STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1972). The *XRAY72* system. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA. Modified by D. SCHWARZENBACH.

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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