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1993 J. Phys.: Condens. Matter 5 6005

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DSC, x-ray diffraction and Raman studies of high-temperature phase transitions in the perovskite-type layer compound butylenediammonium lead tetrachloride

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Received 19 March 1993, in final form 11 May 1993

Abstract. Butylenediammonium lead tetrachloride exhibits three structural phase transitions according to the sequence $\iota - (324 \text{ K}) \rightarrow \gamma - (341 \text{ K}) \rightarrow \beta - (420 \text{ K}) \rightarrow \alpha$. These transitions are characterized by DSC measurements and Raman scattering on polycrystalline samples. The space groups and the cell parameters of ι , γ and β phases were determined by x-ray diffraction on single crystals and powder samples. The three phases ι , γ and β have the same space group $P2_1/c$ with $Z = 4$. The first-order phase transition at 324 K is driven by orientational and conformational motions of the butylenediammonium chains. The transition at 341 K is also of first-order type and involves both organic cation motions and PbCl_6 octahedra deformations. The transition at 420 K was evidenced by Raman scattering; it leads to a plastic phase similar to that observed in the homologous monoammonium compound $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{PbCl}_4$. This transitional behaviour and the crystal dynamics will be discussed and compared with those of homologous compounds.

1. Introduction

The alkylendiammonium tetrachlorometallates of general formula $\text{NH}_3(\text{CH}_2)_n\text{NH}_3\text{MCl}_4$ ($2\text{C}_n\text{MCl}_4$), where M is a divalent metal, are known to crystallize in a two-dimensional structure, built up from corner-sharing MCl_6 octahedra. The cavities between the octahedra contain the NH_3 groups which form $\text{NH}-\text{Cl}$ hydrogen bonds with the chlorine atoms (figure 1) (Blinc *et al* 1977, Negrier *et al* 1987, 1989, Tichy *et al* 1980). These compounds are also known for their numerous structural phase transitions and their complex crystal dynamics. As far as we know, from all previous work on this family of compounds, the organic chains were believed to be responsible for the observed transitions. Their orientational motions and the competition between twisted and *trans* conformations were extensively studied and discussed, but the participation of MCl_6 octahedra was often omitted or neglected (Negrier *et al* 1987, 1989, Tichy *et al* 1980, Sourisseau and Lucazeau 1979, Guillaume *et al* 1990).

Butylenediammonium lead tetrachloride ($2\text{C}_4\text{PbCl}_4$) is a new compound in this family. In a recent article devoted to this compound (Abid *et al* 1991) we described an order-disorder phase transition demonstrated by means of Raman spectroscopy near 200 K. The low-temperature phase below 200 K is believed to be ordered and the organic chains are frozen in different conformations; this has been confirmed by the splitting of the Raman bands at 309 cm^{-1} and 85 cm^{-1} corresponding to the cation motions in four components (Abid *et al* 1991). These results led us to complete this work by studying

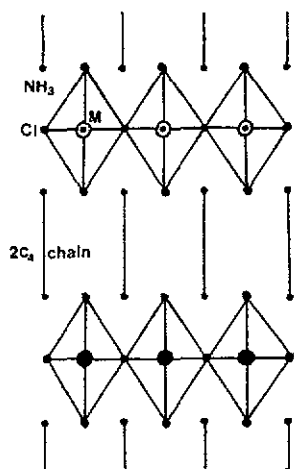


Figure 1. Schematic structure of $2C_nMCl_4$, $n = 2, 3, 4, 5$; $M = \text{Cd}, \text{Mn}, \text{Pb}$ in the hypothetical tetragonal high-temperature phase. The projection is along the a axis. The $2C_n$ chains are more or less parallel to the c axis and perpendicular to the layer planes (after Blinc *et al* 1977 and Negrier *et al* 1987).

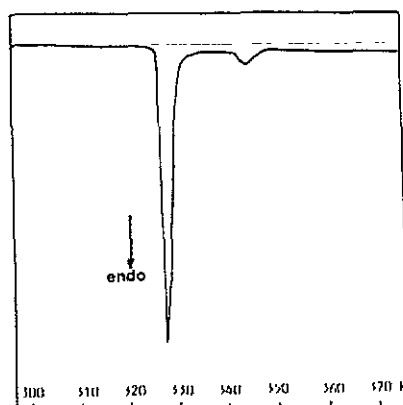


Figure 2. DSC thermogram of $2C_4\text{PbCl}_4$ in the 300–370 K temperature range.

the transitional behaviour in a higher temperature range. In the present work we intend to characterize the high-temperature phases by DSC measurements, x-ray diffraction and Raman scattering between 300 K and 450 K. The transition mechanisms will be discussed and compared with those observed in the homologous compounds $2C_4\text{MnCl}_4$, $2C_4\text{CdCl}_4$ and $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{PbCl}_4$.

2. Experimental details

$2C_4\text{PbCl}_4$ was synthesized by slow evaporation of aqueous solution containing stoichiometric amounts of $\text{NH}_3(\text{CH}_2)_4\text{NH}_3\text{Cl}_2$ and PbCl_4 ; small crystals of about $1 \text{ mm} \times 0.5 \text{ mm} \times 0.3 \text{ mm}$ were selected for x-ray measurements.

Powder x-ray diffraction experiments were performed on a Philips powder counter diffractometer equipped with a home-made heating unit cell, and $\text{Fe K}\alpha$ radiation was used. For single crystals, a precession camera with $\text{Mo K}\alpha$ radiation was used to characterize the crystallographic parameters and space groups of α , γ and β phases. The temperature variations were achieved by means of an Enraf-Nonius air-heated system.

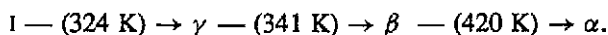
Raman spectra were recorded on a Dilor RTI 30 spectrometer equipped with an argon ion laser (514.5 nm; Spectra Physics, model 2000). A thermocouple was used for temperature measurements.

Calorimetric measurements were performed between 300 and 450 K on a Mettler DSC calorimeter; the recording conditions were a heating rate of 5 K min^{-1} and a sensitivity of $200 \mu\text{V mW}^{-1}$.

3. Results and discussion

3.1. DSC measurements

DSC experiments were performed on heating $2\text{C}_4\text{PbCl}_4$ from 300 K to 450 K. The thermogram shows two endothermic peaks at $T_1 = 324$ K and $T_2 = 341$ K (figure 2). The enthalpy and entropy changes are respectively $\Delta H_1 = 1.1$ kJ mol⁻¹, $\Delta S_1 = 3.4$ J mol⁻¹ K⁻¹, and $\Delta H_2 = 0.08$ kJ mol⁻¹, $\Delta S_2 = 0.23$ J mol⁻¹ K⁻¹; they are of the same order of magnitude as those measured for the first-order transitions in similar compounds: $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{PbCl}_4$ (Romain *et al* 1992) and $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{MnCl}_4$ (Depmeier *et al* 1977). Both transitions are thus considered to be of the first-order type. It should be noticed that above 350 K no thermal anomalies have been observed in the thermogram, although a third transition near 420 K was detected by Raman scattering (see section 3.3). By analogy with the nomenclature used for homologous compounds the high-temperature phases have been named γ , β and α (Romain *et al* 1992, Depmeier *et al* 1977), the Γ phase is that existing at 300 K (Abid *et al* 1991):



For the $\Gamma \rightarrow \gamma$ transition, the relation $\Delta S = R \ln \Omega$ brings to a number of equivalent positions $\Omega = 1.5$; this value means that the relative disorder of the γ phase is of complex nature, and probably reflects a conformational modification of organic chains rather than a statistical distribution of atoms between different positions.

3.2. X-ray experiments

For phase α , the precession patterns obtained above 420 K apparently show an orthorhombic symmetry but the extinction conditions are not reproducible and no correct space group has been found; this may be due to the crystal instability above 420 K. The following crystallographic study was thus restricted to the Γ , γ and β phases. However, the Raman study shows a strong analogy between the α phase and the disordered phases evidenced in the homologous compounds. This point will be discussed below.

3.2.1. Γ phase. Precession photographs have been taken at 300 K and the following reflection conditions have been noticed:

$$\begin{aligned} (h0l) & \quad l = 2n \\ (0k0) & \quad k = 2n \\ (hkl) & \quad \text{no conditions.} \end{aligned}$$

These correspond unambiguously to the $P2_1/c$ space group. Approximate values of the cell parameters obtained from precession patterns have been refined through the observed reflections on the powder data (table 1); the retained values are

$$a = 7.934(1) \text{ \AA} \quad b = 7.796(2) \text{ \AA} \quad c = 19.724(3) \text{ \AA} \quad \beta = 94.6(4)^\circ.$$

The structure determination of the title compound at room temperature is in progress (Daoud *et al*), although some structural information should be presented here for comparison

Table 1. Indexing of the powder diagram (22 observed reflections) in the monoclinic room-temperature phase α , at 300 K.

No	d_{cal} (Å)	d_{obs} (Å)	hkl	I/I_{max}
1	9.829	9.837	002	20
2	5.931	5.934	102	100
3	5.552	5.549	110	6
4	5.552	5.549	11 $\bar{1}$	7
5	4.424	4.424	111	61
6	4.956	4.959	11 $\bar{2}$	11
7	4.914	4.919	004	17
8	4.720	4.719	112	8
9	4.157	4.159	11 $\bar{4}$	16
10	4.122	4.120	113	16
11	4.030	4.034	104	5
12	3.892	3.899	020	6
13	3.776	3.779	20 $\bar{2}$	5
14	3.398	3.399	21 $\bar{2}$	61
15	3.276	3.279	006	6
16	3.054	3.059	20 $\bar{4}$	5
17	2.965	2.963	204	6
18	2.802	2.804	124	18
19	2.772	2.770	214	7
20	2.535	2.529	215	40
21	2.508	2.499	02 $\bar{6}$	19
22	2.038	2.040	315	81

of organic chain and MCl_6 octahedra distortions in $2\text{C}_4\text{PbCl}_4$ with those in $2\text{C}_4\text{CdCl}_4$ and $2\text{C}_4\text{MnCl}_4$.

At 300 K, the preliminary structural determination of $2\text{C}_4\text{PbCl}_4$ shows that the butylenediammonium chains are distorted: the C–C bonds and C–N bonds are not in the same plane (twisted conformation). On the other hand the PbCl_6 octahedra exhibit nearly the same distortion as that observed in $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{PbCl}_4$ (Meresse and Daoud 1989). Indeed, the Pb–Cl axial bonds (out-of-layer plane) are bent, with an angle $\text{Cl}_{\text{ax}}\text{–Pb–Cl}_{\text{ax}} = 165^\circ$ instead of 180° , and in addition the in-plane $\text{Cl}_{\text{eq}}\text{–Cl}_{\text{eq}}$ distance varies from 3.80 to 4.30 Å, a fact which is observed also in the Cd derivative $2\text{C}_4\text{CdCl}_4$ (Blinc *et al* 1977, Walpen 1976) and in $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{PbCl}_4$ mentioned above.

3.2.2. γ and β phases. For γ and β phases, precession photographs show the same reflection conditions as those of the α phase. They exhibit unambiguously the same space group, $P2_1/c$ with $Z = 4$. This result has been confirmed by the indexing of the powder data at 330 K (γ) and 360 K (β). The cell parameters obtained after the least-squares refinement are summarized in table 2. This crystallographic evolution is similar to that observed in the homologous compound $2\text{C}_4\text{CdCl}_4$, which exhibits three monoclinic phases preceding the orthorhombic one above 371 K (Blinc *et al* 1977, Walpen 1976).

Table 2. Crystallographic characterization of α , γ and β phases.

	a (Å)	b (Å)	c (Å)	β (°)	Z
α	7.934(1)	7.796(2)	19.724(3)	94.6(4)	4
γ	8.004(2)	7.744(3)	19.955(5)	97.0(4)	4
β	8.057(3)	7.754(4)	20.084(3)	101.9(2)	4

As is shown in table 2 only the c parameter and the β angle are noticeably affected by the $\text{I} \rightarrow \gamma$ and $\gamma \rightarrow \beta$ transitions while a and b remain almost unmodified. The thermal expansion along the c axis corresponding to the interlayer distance, in particular across the $\text{I} \rightarrow \gamma$ transition, may be explained as follows. It has already been mentioned that at room temperature, the proportion of twisted chains is dominant; as we will see below, when increasing the temperature the proportion of *trans* chains increases at the expense of the twisted ones and becomes dominant at high temperature. As the *trans* chains are significantly longer than the twisted ones, the interlayer distance and therefore the parameter c must increase. A similar phenomenon was observed in $2\text{C}_4\text{CdCl}_4$ (Blinic *et al* 1977, Walpen 1976), whereas in $2\text{C}_4\text{MnCl}_4$ and $2\text{C}_5\text{CdCl}_4$ the opposite phenomenon was evidenced: the interlayer distance decreases with increasing temperature because the proportion of twisted chains is dominant in the high-temperature phases (Negrier *et al* 1987, 1989, Tichy *et al* 1980).

3.3. Raman spectroscopy

3.3.1. Assignments. Raman spectra of polycrystalline samples of $2\text{C}_4\text{PbCl}_4$ have been recorded at different temperatures between 300 and 450 K only in the 5–250 cm^{-1} and 400–1200 cm^{-1} frequency ranges. The first spectral domain includes the lattice modes, which are generally the most sensitive to phase transitions and give rise to the most intense bands throughout the spectrum. The 400–1200 cm^{-1} domain includes stretching and deformation modes of the N–C–C–C–N skeleton, which are sensitive to conformational changes.

The frequencies of the observed modes in different phases are listed in table 3. We do not intend to give here a detailed assignment, but we intend as far as possible to distinguish between the bands corresponding to the PbCl_6 octahedra motions and those associated with the 2C_4 chains. To this end we have recorded the spectrum of the Cd derivative $2\text{C}_4\text{CdCl}_4$. Comparing the spectra of figure 3, it appears clearly that the bands at 18, 35 and 131 cm^{-1} are characteristic of $2\text{C}_4\text{PbCl}_4$ spectra; these are assigned to PbCl_6 octahedra motions, whereas the common bands in both spectra, near 45, 62, 85 and 95 cm^{-1} , are assignable to 2C_4 chain motions; these bands have different intensities and widths in the two spectra (figure 3); this may be related to different degrees of disorder in the compounds. As we will see below, the bands at 85 and 95 cm^{-1} have a competition behaviour when increasing the temperature, according to the distortion of 2C_4 chains observed by x-ray diffraction and by analogy with the homologous compounds, namely $2\text{C}_4\text{CdCl}_4$ and $2\text{C}_5\text{CdCl}_4$ (Negrier *et al* 1987); the intense band at 85 cm^{-1} and the shoulder at 95 cm^{-1} may be associated with the twisted and *trans* conformers respectively. The difference between their relative intensities indicates that at room temperature (I phase) the proportion of twisted chains is highly dominant.

The assignment of the internal modes in the 400–1200 cm^{-1} range has been established by comparison with the spectra of Cd derivatives; they are at almost the same frequencies in all aliphatic chains (see, for example, Delarbre *et al* 1989, Durig *et al* 1989). The most interesting bands in this spectral domain are those at 425, 936 and 963 cm^{-1} , which are sensitive to conformational competition of 2C_4 chains.

3.3.2. Transition characterization and crystal dynamics. The spectral evolution with increasing temperature is shown in figures 4 and 5. Both transitions, at 324 K and 341 K, are clearly characterized. In addition, a new phase transition is evidenced at about 420 K.

(a) $\text{I} \rightarrow \gamma$ transition (324 K). When increasing the temperature from phase I to phase γ , the spectral modifications concern both external and internal modes of the organic chains.

Table 3. Raman spectral wavenumbers (in the 10–220, 400–480 and 900–1050 cm^{-1} ranges) at different temperatures. w = weak; m = medium; s = strong; sh = shoulder.

Γ	$\xrightarrow{324 \text{ K}}$ γ	$\xrightarrow{341 \text{ K}}$ β	$\xrightarrow{420 \text{ K}}$ α	Assignment
314 K	338 K	348 K	430 K	
18 w	18 w	—	—	PbCl ₆
35 m	35 m	—	30 m	PbCl ₆
46 s	46 sh	48 sh	—	(2C ₄)
49 sh	50 s	51 s	—	PbCl ₆
62 s	62 s	63 s	50 m	(2C ₄)
85 s	85 m	—	—	R'2C ₄ (twisted)
—	95 sh	97 s	—	R'2C ₄ (<i>trans</i>)
—	—	115 m	—	—
131 m	130 m	130 sh	—	ν (ClPbCl)
181 m	181 m	181 w	—	(2C ₄)
425 m	423 m	422 w	—	δ CCCC (twisted)
450 w	446 m	445 s	—	δ CCCC (<i>trans</i>)
470 m	470 m	474 w	—	—
936 s	939 s	937 m	—	ν CC (twisted)
963 w	965 m	960 w	—	ν CC (<i>trans</i>)
990 m	991 s	994 s	995 w	rocking (CH ₂)
1036 m	1036 m	1036 m	1036 w	rocking (CH ₂)
—	1042 m	—	—	—

Indeed, the intensities of the bands at 95, 450 and 963 cm^{-1} associated with the *trans* conformer strongly increase with respect to those at 85, 425 and 936 cm^{-1} respectively, associated with the twisted conformation (figures 4 and 5). This means that in phase Γ the proportion of twisted chains is highly dominant; when increasing the temperature across the $\Gamma \rightarrow \gamma$ transition, competition between twisted and *trans* conformers takes place.

On the other hand, the band at 35 cm^{-1} assigned to PbCl₆ rotation and that at 131 cm^{-1} corresponding to Cl–Pb–Cl stretching remain almost unmodified in the $\Gamma \rightarrow \gamma$ transition, and we can conclude that the $\Gamma \rightarrow \gamma$ transition is of the first order–disorder type and involves mainly the orientational and conformational dynamics of the organic chains. This interpretation is consistent with previous results inferred from calorimetric and crystallographic data. While the transition occurs, the PbCl₆ octahedron framework remains practically the same and the $P2_1/c$ space group is preserved.

(b) $\gamma \rightarrow \beta$ transition (341 K). This transition is characterized by drastic modifications in the low-frequency spectra; it is also of first-order type. When heating the sample from the γ to the β phase the weak lines at 95, 450 and 963 cm^{-1} associated with the *trans* chains grow progressively in intensity. When the β phase occurs they become more intense than those of the twisted chains at 85, 425 and 936 cm^{-1} (figures 4 and 5). This spectral evolution indicates that the conformational equilibrium between *trans* and twisted states of the chains is progressively displaced in favour of the *trans* conformation, and when the β phase occurs the organic chains are practically exclusively in the *trans* conformation. Also, the γ phase seems to be only an intermediate state between Γ and β crystalline structures with a continuous evolution of twisted–*trans* equilibrium according to the temperature. This is in agreement with the increasing of the interlayer distance already observed by x-ray diffraction. Similar results on chain conformational disorder have been obtained for a number of compounds in this family, namely 2C₅MnCl₄, 2C₅CdCl₄, 2C₄CdCl₄ and 2C₄MnCl₄ (Blinc *et al* 1977, Negrier *et al* 1987, 1989, Sourisseau *et al* 1983, Tichy *et al* 1980). On the other hand, the spectral evolution shows that the conformational motions are coupled with PbCl₆ octahedra deformations. Indeed, the bands at 18 and 35 cm^{-1} assigned

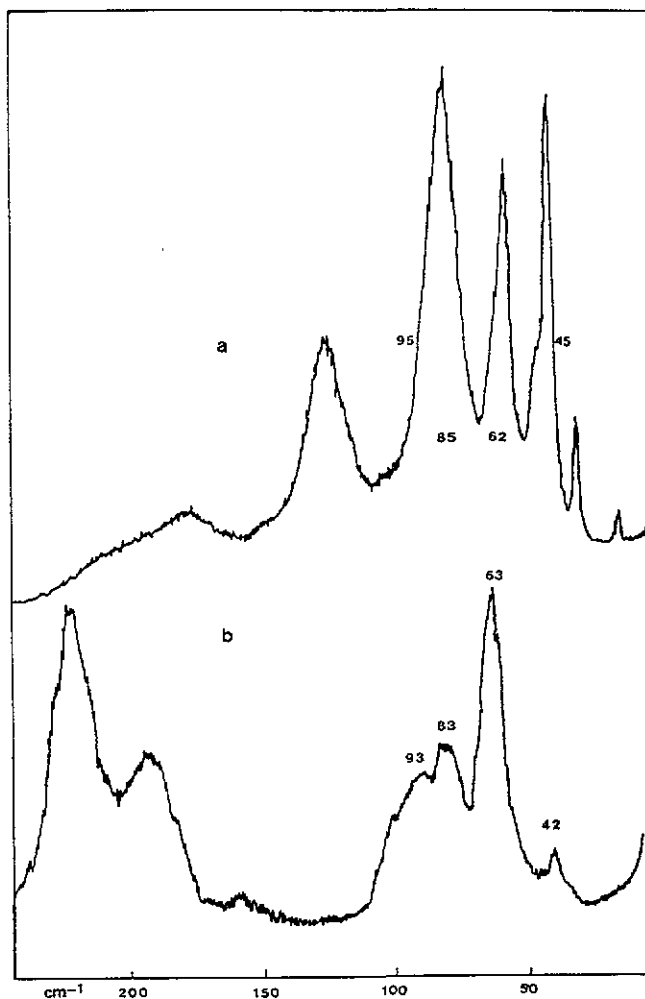


Figure 3. Low-frequency Raman spectra of polycrystalline samples of $2\text{C}_4\text{PbCl}_4$ (spectrum a) and $2\text{C}_4\text{CdCl}_4$ (spectrum b) at room temperature.

to PbCl_6 libration vanish and the band at 130 cm^{-1} assigned to Cl-Pb-Cl stretching shows a large broadening; such a behaviour of these dispersive modes in phase β reflects the degree of disorder in the Cl sublattice and the displacive character of the $\gamma \rightarrow \beta$ transition. This disorder must induce some modifications in $\text{NH}\dots\text{Cl}$ bonding schemes and therefore generates favourable orientations and conformations of the organic chains.

(c) $\beta \rightarrow \alpha$ transition (420 K). In phase α , the spectrum is totally different from the previous ones. In particular, the bands at 50 , 62 and 181 cm^{-1} vanish, while a broad and relatively intense band appears at 30 cm^{-1} ; the latter was also observed in the plastic phase (α) of $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{PbCl}_4$ and is assigned to the 'rotations' of PbCl_6 octahedra around their axes perpendicular to the layer planes (Romain *et al* 1992); on the other hand the Cl-Pb-Cl stretching band vanishes and shows a large broadening near 117 cm^{-1} ; this spectroscopic behaviour is close to that observed in the α plastic phase of $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{PbCl}_4$ and other plastic phases in which there exists a dynamic rotational disorder (Romain *et al* 1992, Sherwood 1979). These noticeable and abrupt changes in a relatively narrow temperature

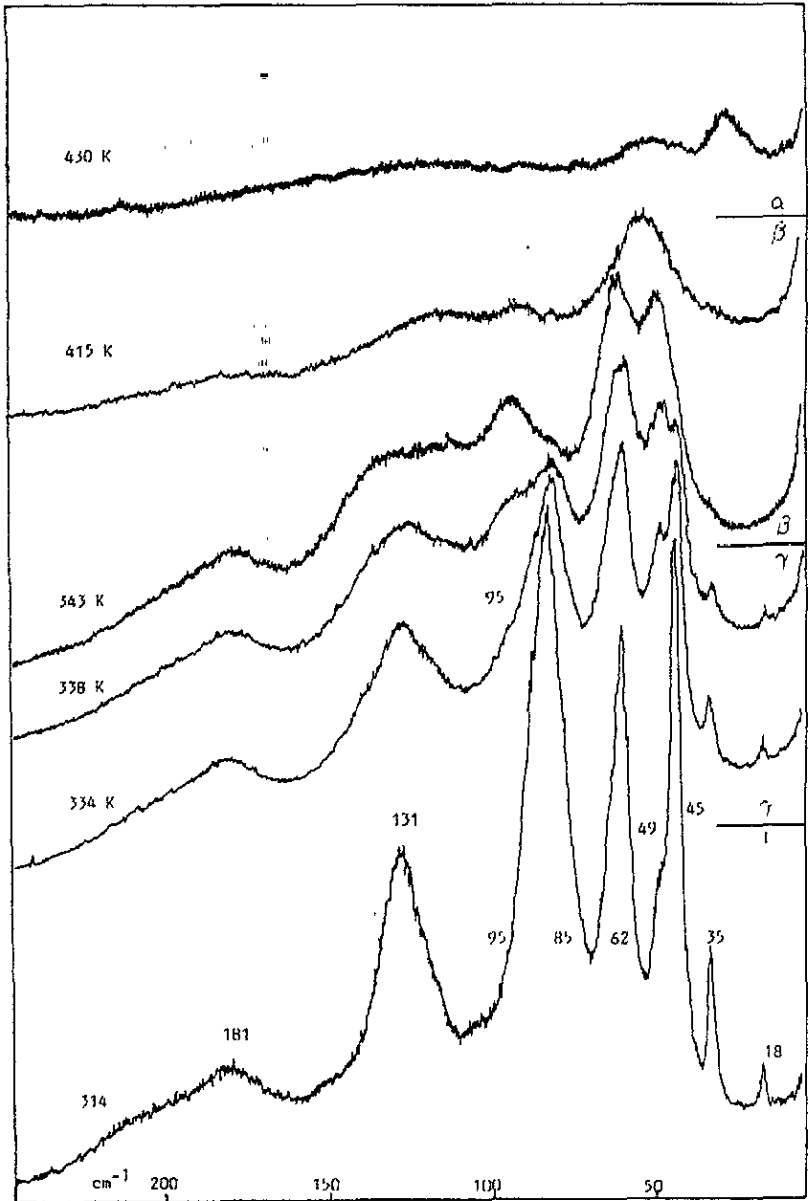


Figure 4. Low-frequency Raman spectra of a polycrystalline sample of $2C_4PbCl_4$ at various temperatures between 300 and 450 K.

range (415–340 K) suggests probably a first-order character for this transition.

The spectral evolution across the $\beta \rightarrow \alpha$ transition can be explained as follows. The increasing temperature from β to α generates a high degree of disorder in the Cl sublattice and induces inhomogeneities in the potential wells for NH_3 groups. This gives rise firstly to an anharmonic behaviour for $2C_4$ chain vibrators and secondly to the breakdown of the translational symmetry, and therefore to the appearance of the density of states for coupled $PbCl_6$ vibrators. This can explain the shape of the spectra in the disordered α phase.

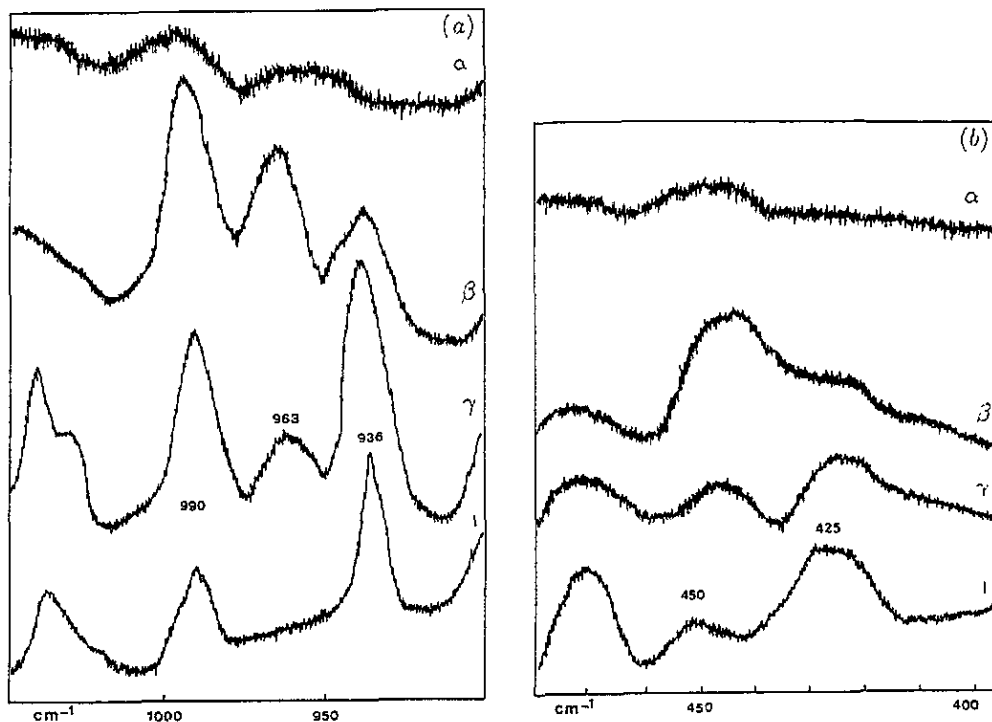
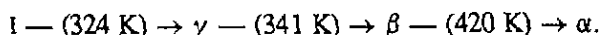


Figure 5. Raman spectra of different phases of $2\text{C}_4\text{PbCl}_4$: (a), between 400 and 480 cm^{-1} ; (b), between 900 and 1050 cm^{-1} .

4. Concluding remarks and comparison with homologous compounds

The title compound exhibits three phase transitions:



The I, γ and β phases exhibit monoclinic cell symmetry; the α phase is apparently orthorhombic. The $\text{I} \rightarrow \gamma$ transition is of order-disorder type and involves only organic chain dynamics. The subsequent $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions would be driven by a displacive mechanism in which PbCl_6 octahedra participate strongly together with 2C_4 chains. The crystallographic evolution and transitional mechanisms are similar to those observed for $2\text{C}_4\text{CdCl}_4$. This similarity is apparently related to the strong distortion of PbCl_6 and CdCl_6 octahedra.

From the point of view of conformational disorder and octahedron distortion, two types of compound can be distinguished in this family:

(i) When the MCl_6 octahedra are undistorted, at room temperature, the proportion of *trans* chains is dominant; when the temperature is increased the equilibrium between twisted and *trans* conformations is displaced in favour of twisted ones; this is the case in $2\text{C}_4\text{MnCl}_4$ (Tichy *et al* 1980) and $2\text{C}_5\text{CdCl}_4$ (Negrier *et al* 1987, 1989).

(ii) When the octahedra are strongly distorted, the opposite phenomenon takes place and the *trans* conformation becomes dominant in high-temperature phases; this is the case in $2\text{C}_4\text{PbCl}_4$ (present work) and $2\text{C}_4\text{CdCl}_4$ (Blinic *et al* 1977).

Acknowledgments

The authors wish to thank Dr Daoud for chemical synthesis of the samples and for fruitful suggestions.

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