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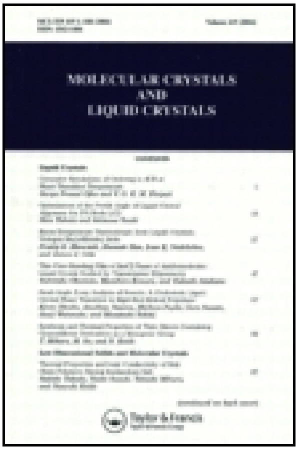

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Thermal Behaviour and Room Temperature Crystal Structure of a Bidimensional Complex Salt of 4-Aminocinnamic Acid and Cadmium Chloride

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Thermal Behaviour and Room Temperature Crystal Structure of a Bidimensional Complex Salt of 4-Aminocinnamic Acid and Cadmium Chloride

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The crystal structure at room temperature of the complexe salt 4-aminocinnamic acid cadmium chloride $(HOOC—CH{=}CH—(C_6H_4)—NH_3)_2\,CdCl_4$ has been solved by X-ray diffraction method. The structure exhibits bidimensional arrangement with alternated inorganic-organic layers, in a monoclinic symmetry $P2_1/m$: a = 0.5389(1) nm; b = 3.0165(7) nm; c = 0.6999(3) nm; β = 104.09(3)°. Structural considerations allow to explain the photoinactivity (polymerization) of the compound at room temperature upon irradiation with UV light in contrast to some similar butadiene derivatives which undergo a stereospecific 1, 4-addition reaction. Thermal investigations by powder X-ray diffraction and calorimetric methods show during heating process, an exothermic irreversible transformation in the solid state at high temperature concurrently with the disappearance of the tridimensional organization in the structure. A complete interpretation of this phenomenon needs further complementary investigation.

Keywords: Bidimensional complex; Photoreactivity; Crystal structure

I. INTRODUCTION

Organic-inorganic complex crystals such as the perovskite-type layer compounds with general formula $(C_nH_{2n+1}NH_3)_2\,MX_4$ (where M = Mn, Cd, Cu and X = Cl,

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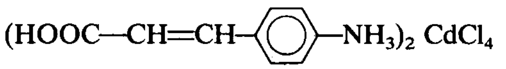
Br) received considerable interest recently, because they can exhibit quasi two-dimensional magnetic properties[1] and undergo numerous structural phase transitions (2–6 and References cited therein). Recently, it was been demonstrated that these compounds may serve as matrices for chemical reactions occurring within the organic layers.[7,8] For example, the butadiene derivatives are able to undergo a stereospecific 1,4-addition reaction (polymerization) if exposed to UV or γ irradiation.[9] While the complex salts of saturated primary amines were studied in great detail, the corresponding salts of unsaturated amines or anilines are less intensively investigated. We are interested in the study of the complex salt of 4-aminocinnamic acid and cadmium chloride:


(1)

which was reported not to show the expected (2 + 2)-cyclo addition upon irradiation with UV light.[7] Purpose of the present paper is to report the crystal structure of the complex determined by X-ray diffraction at room temperature which allows to point out the reasons of the photoinactive properties of this compound and to report the thermal behaviour of the compound which has also been investigated in the range 100–523 K by X-ray powder diffraction and differential scanning calorimetry.

II. EXPERIMENTAL

The hydrochloride of 4-aminocinnamic acid was purchased from Aldrich Co and used after recrystallization from 1 molar hydrochloric acid. For the preparation of the complex crystals (1), 10 mmoles of the hydrochloride salt were dissolved in 20 ml of hot 0.1 molar aqueous HCl and treated with 6 ml of hot aqueous $CdCl_2$ solutions (conc. 1 mole/l). Upon cooling and evaporation of water, small yellowish platelets were formed, which were filtered off, dried and used for X-ray structure analysis without further treatment. An analysis of the chemical compound† has been made by the determination of C, H, N, Cl, Cd contents (Table I).

Weissenberg photographs showed the space group to be either $P2_1$ or $P2_1/m$; the latter was confirmed during the structure refinement. Lattice parameters were obtained from least-squares adjustement of the setting angles of 25 reflections with

TABLE I

%	C	N	H	Cl	Cd
exp	37.40	3.50	4.77	24.36	19.75
calc.	37.09	3.43	4.80	24.38	19.30

---

†Realized by Service Central d'Analyse du Centre National de Recherche Scientifique, 69390 Vernaison (France).

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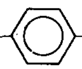
TABLE II

Summary of crystal data, intensity collection and structure refinement

Formula	[HOOC—CH=CH——NH$_3$]$_2$ CdCl$_4$
Molecular mass	582.58
Dimensions	0.05 × 0.30 × 0.45 mm
Crystal system	Monoclinic
Space group	P2$_1$/m
a(Å)	5.389(1)
b(Å)	30.165(7)
c(Å)	6.999(3)
β(°)	104.09(3)
Z	2
d_{calc}	1.76
F_{000}	580
μ(cm^{-1})	129.6
Radiation	CuK$_\alpha$ (graphite monochromator)
Min/Max transmission	0.19/0.99
Scan method	$\omega - 2\theta$
Background from	scan profile interpretation
(sin θ/1)max	0.61 Å-1
Data collected	1/4 sphere
Number of unique reflections	2161
Number of reflections (I > 3σ)	1948
Nb of reflect/Nb of paramet.	15
Resolution method	Patterson and Fourier
Refinement method	Block diagonal least-squares
Function minimized	$\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
ω	$1/\sigma^2$
R (R_w)	0.074 (0.070)
goodness of fit	1.23

$9 < \theta < 60°$. Intensity data were collected with Enraf Nonius CAD-4 diffractometer, graphite monochromator, CuK radiation, ($\omega - 2\theta$) scan, range of hkl: h from -6 to 6, k from 0 to 36, 1 from 0 to 8. Empirical absorption correction was applied to the measured intensities, transmission factors ranged from 0.19 to 0.99. Three monitored reflections ($\bar{1}$ 2 2, 2 5 1, 2 7 1) observed after every 100 collected reflections showed no change in intensities during the measurement. Table II summarizes the crystallographic data and data collection procedure. The structure was determined by heavy-atom and Fourier techniques. Atomic scattering factors were from International Tables For X-ray Crystallography,[10] except for hydrogen atoms (Stewart, Davidson & Simpson[11]). Anomalous dispersion factors were applied to Cd and Cl. The H atoms were located and refined isotropically. The structure was refined with $w = 1$ if $F_o < p$ and $w = p^2/F_o^2$ if $F_o > p$ where $p = (F^2_{omax}/10)^{1/2}$ to $R = 0.074$, $wR = 0.070$ and $S = 1.23$.†

The calculations were carried out with local programs CRISAFFI and CRISUTIL on a Mini 6/92 Bull Computer, the positional parameters of the atoms are reported on Table III; the anisotropic thermal factors in Table IV. The bond lengths and

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†The list of observed and calculated structure factors could be obtained from Dr. N. B. Chanh, Laboratoire de Cristallographie, Université Bordeaux I, 44305—Talence (France).

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TABLE III

Final positional parameters and equivalent isotropic thermal factors
($B_{eq} = 4/3 \Sigma \Sigma \beta_{ij} a_i a_j$)

	X	*Y*	*Z*	B_{eq}
C*d* (1)	0.3603 (2)	0.2500 (0)	0.5114 (1)	3.0 (0)
CL (2)	0.2861 (4)	0.1739 (1)	0.3658 (3)	3.5 (1)
CL (3)	0.8229 (6)	0.2500 (0)	0.4614 (5)	3.6 (1)
CL (4)	0.4067 (6)	0.2500 (0)	0.8739 (5)	3.9 (1)
N (21)	−0.2925 (13)	0.1721 (3)	1.1262 (10)	3.6 (3)
C (11)	−0.2740 (15)	0.1432 (3)	0.9629 (12)	3.2 (3)
C (12)	−0.4207 (16)	0.1052 (3)	0.9239 (13)	3.8 (4)
C (13)	−0.3999 (16)	0.0790 (3)	0.7686 (13)	3.8 (4)
C (14)	−0.2299 (16)	0.0896 (3)	0.6516 (12)	3.4 (3)
C (15)	−0.0844 (17)	0.1288 (3)	0.6978 (12)	3.7 (4)
C (16)	−0.1073 (16)	0.1554 (3)	0.8515 (12)	3.6 (4)
C (24)	−0.2082 (17)	0.0616 (3)	0.4905 (13)	3.9 (4)
C (25)	−0.0271 (17)	0.0641 (3)	0.3900 (13)	3.9 (4)
C (26)	−0.0198 (17)	0.0349 (3)	0.2239 (13)	4.0 (4)
O (27)	−0.1933 (12)	0.0066 (2)	0.1601 (9)	4.7 (3)
O (28)	0.1715 (12)	0.0409 (3)	0.1469 (10)	5.5 (4)
H (112)	−0.5410 (151)	0.0968 (31)	1.0049 (113)	4.8
H (113)	−0.5034 (138)	0.0510 (31)	0.7365 (110)	5.0
H (115)	0.0340 (148)	0.1373 (31)	0.6157 (109)	5.2
H (116)	−0.0018 (145)	0.1829 (31)	0.8850 (109)	5.4
H (124)	−0.3429 (136)	0.0381 (31)	0.4430 (111)	5.0
H (125)	0.1125 (137)	0.0874 (31)	0.4296 (110)	5.1
H (121)	−0.3204 (137)	0.2034 (30)	1.0779 (107)	5.6
H (221)	−0.1273 (139)	0.1701 (31)	1.2402 (112)	5.1
H (321)	−0.4438 (141)	0.1622 (31)	1.1783 (112)	5.1
H (128)	0.2047 (133)	0.0206 (32)	0.0553 (110)	5.5

TABLE IV

Anisotropic thermal factors, expressed in the following form: ($\times 10^{-4}$)
$\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$

	β11	β22	β33	β12	β13	β23
C*d* (1)	322 (3)	6 (0)	183 (2)	0 (0)	165 (4)	0 (0)
CL (2)	312 (8)	8 (0)	263 (6)	−14 (2)	253 (12)	−16 (2)
CL (3)	304 (12)	8 (0)	247 (9)	0 (0)	193 (17)	0 (0)
CL (4)	432 (15)	10 (0)	169 (7)	0 (0)	115 (18)	0 (0)
N (21)	365 (31)	10 (1)	194 (18)	3 (9)	198 (40)	−16 (7)
C (11)	341 (35)	8 (1)	175 (20)	13 (10)	192 (45)	1 (8)
C (12)	361 (38)	10 (1)	231 (24)	−9 (11)	249 (51)	−3 (9)
C (13)	390 (40)	9 (1)	213 (23)	−30 (11)	146 (51)	−7 (8)
C (14)	351 (36)	7 (1)	200 (22)	4 (10)	115 (47)	3 (8)
C (15)	450 (42)	8 (1)	197 (22)	−16 (11)	276 (52)	5 (8)
C (16)	400 (39)	9 (1)	198 (22)	−16 (11)	278 (50)	−18 (8)
C (24)	422 (41)	9 (1)	212 (23)	−6 (11)	180 (53)	−10 (9)
C (25)	431 (41)	9 (1)	207 (23)	9 (11)	189 (52)	−23 (9)
C (26)	413 (41)	9 (1)	234 (24)	0 (11)	228 (53)	−4 (9)
O (27)	550 (33)	10 (1)	272 (19)	−40 (9)	379 (42)	−35 (7)
O (28)	551 (34)	14 (1)	353 (22)	−38 (10)	512 (46)	−66 (9)

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angles of the inorganic part, the organic molecule and of the hydrogen bond region are given in Table V. The projection of the structure along the c axis (Figure 1) shows the characteristic features of each inorganic and organic component.

III. CRYSTAL STRUCTURE ANALYSIS

a) General features

The results show clearly a bidimensional arrangement with an organic part made of 4-aminocinnamic acid molecules embedded in an inorganic ($CdCl_4$) matrix, forming an alternated inorganic-organic layered structure.

The crystalline cohesion in the $\vec{b}$ direction perpendicular to the layers is achieved by means of two types of hydrogen bonds. On the one hand, the connection between the inorganic ($CdCl_4$) layer and the NH_3 group of the molecule is realized through three (N—H . . . Cl) hydrogen bonds. On the other hand, in side the molecular layer, two molecules of 4-aminocinnamic acid are linked each to other by two (O—H . . . O) hydrogen bonds, forming a double carboxylic bridge around a symmetry center.

The crystalline cohesion in the direction ($\vec{a}$, $\vec{c}$) parallel to the layer is achieved

TABLE V

Interatomic distances (10^{-1} nm) and angles (°)

Cd(1)-Cl(2)	2.504 (2)	Cl(2)-Cd(1)-Cl(3)	90.50(12)	inorganic part
Cd(1)-Cl(3)	2.600 (2)	Cl(2)-Cd(1)-Cl(2)iiii	132.95(14)	
Cd(1)-Cl(4)	2.488 (2)	Cl(2)-Cl(3)-Cl(4)	65.02(10)	
Cd(1)-Cl(3)i	2.831 (2)	Cl(2)-Cl(3)-Cl(2)iiii	78.60(11)	
		Cl(2)-Cl(3)ii-Cl(2)iiii	80.00(12)	
		Cl(2)-Cl(3)ii-Cl(4)	69.39(11)	
N(21)-C(11)	1.461(10)	N(21)-C(11)-C(12)	120.39(69)	organic part
C(11)-C(12)	1.381(11)	N(21)-C(11)-C(16)	117.43(68)	
C(11)-C(16)	1.376(11)	C(12)-C(11)-C(16)	122.18(74)	
C(12)-C(13)	1.370(12)	C(11)-C(12)-C(13)	118.78(76)	
C(15)-C(16)	1.372(12)	C(11)-C(16)-C(15)	118.85(75)	
C(13)-C(14)	1.406(11)	C(12)-C(13)-C(14)	121.44(76)	
C(14)-C(15)	1.412(11)	C(16)-C(15)-C(14)	121.28(75)	
C(14)-C(24)	1.436(11)	C(13)-C(14)-C(15)	117.46(72)	
C(24)-C(25)	1.337(12)	C(13)-C(14)-C(24)	120.82(70)	
C(25)-C(26)	1.468(12)	C(15)-C(14)-C(24)	121.72(72)	
C(26)-O(27)	1.263(10)	C(14)-C(24)-C(25)	126.09(77)	
C(26)-O(28)	1.287(11)	C(24)-C(25)-C(26)	123.11(77)	
		C(25)-C(26)-O(27)	121.72(75)	
		C(25)-C(26)-O(28)	115.20(74)	
		O(27)-C(26)-O(28)	123.07(78)	
N(21)H-Cl(2)iii	3.135 (7)	C(11)-N(21)-Cl(2)iii	128.64(46)	inorganic organic region
N(21)H-Cl(2)i	3.160 (7)	C(11)-N(21)-Cl(4)ii	97.56(43)	
N(21)H-Cl(4)ii	3.142 (7)	C(11)-N(21)-Cl(3)iii	162.41(48)	
N(1)H-Cl(3)iii	3.271 (7)			

Symmetry code: (i) $x + 1, y, z$; (ii) $x - 1, y, z$; (iii) $x - 1, y, z + 1$;
(iiii) $x, 1/2 - y, z$

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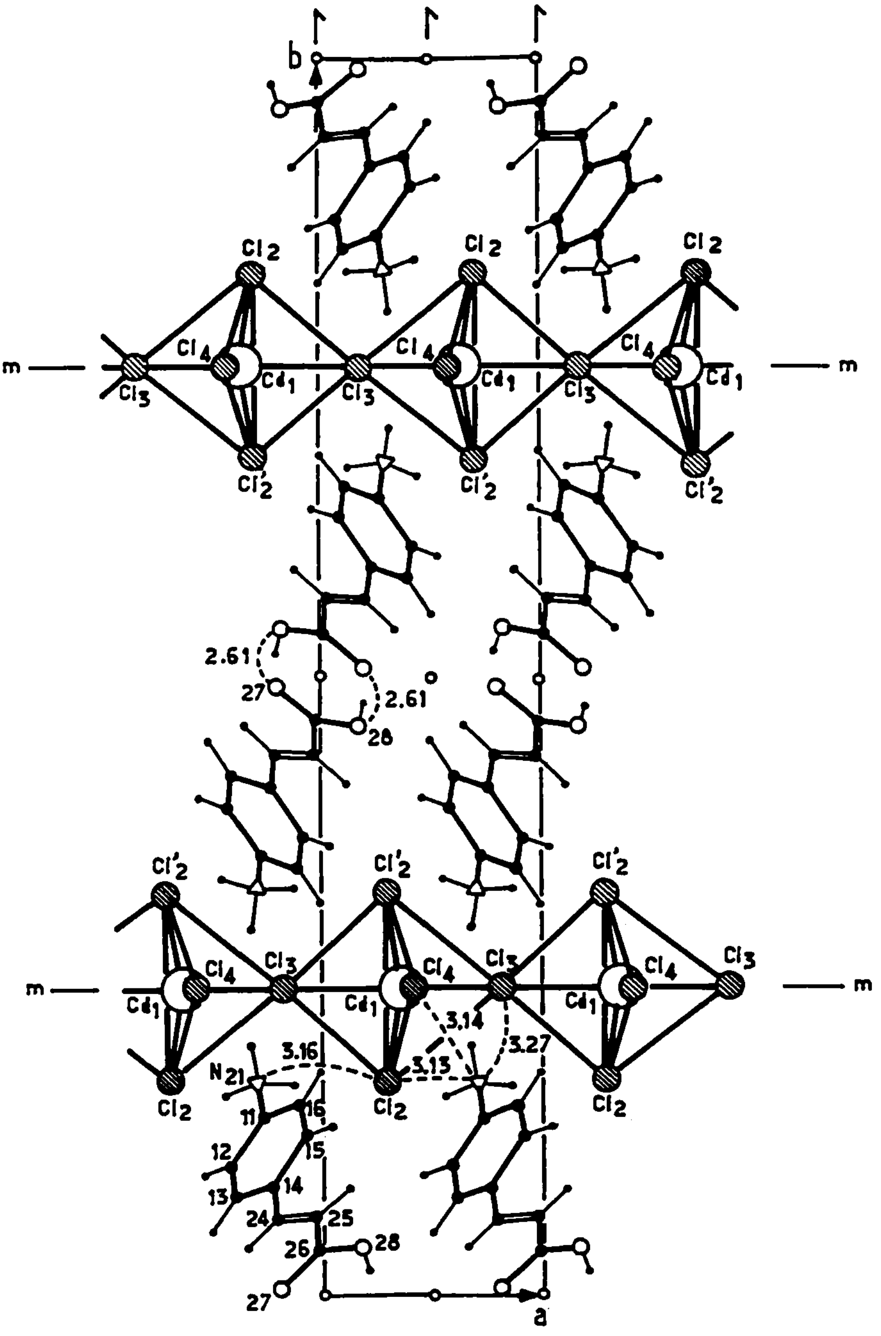

FIGURE 1 Projection of the structure along $\vec{c}$ axis.

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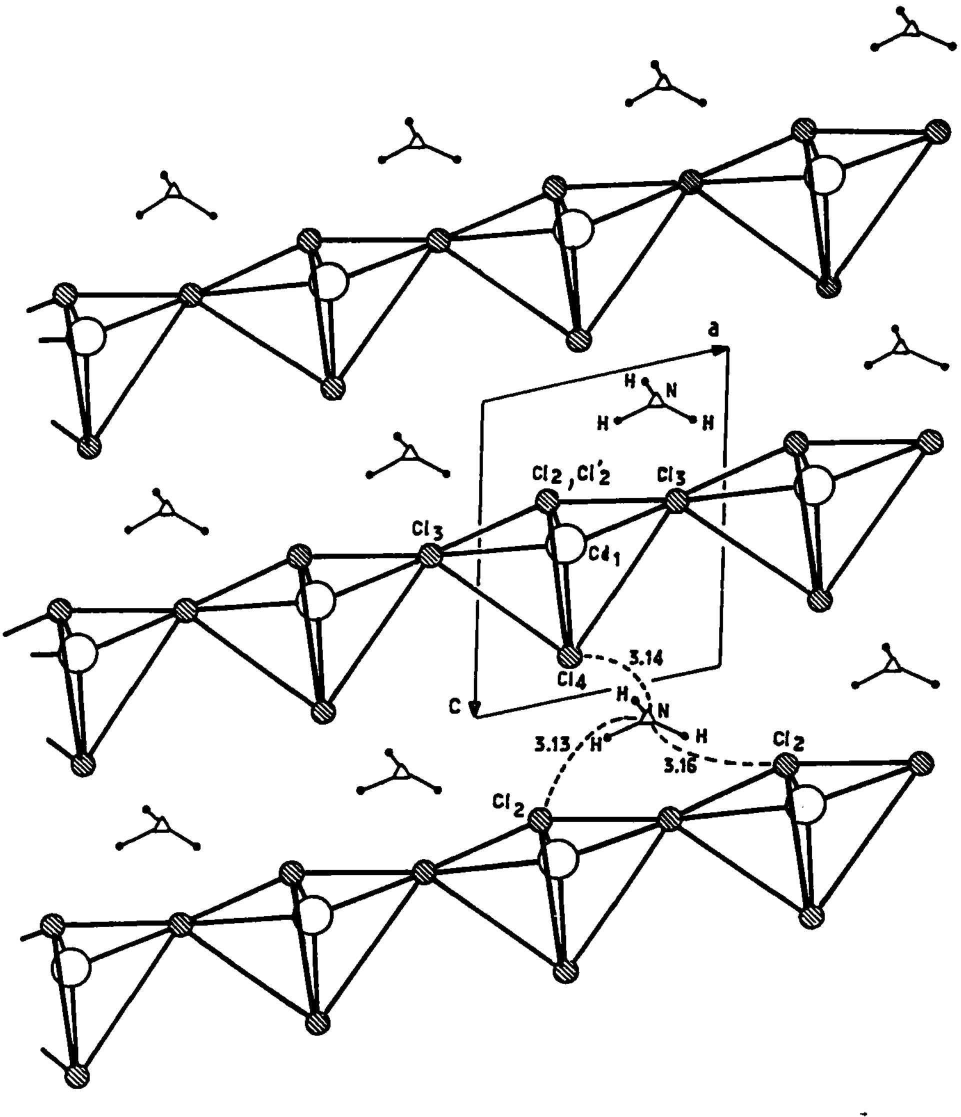

FIGURE 2 Hydrogen bond region viewed on the projection of the structure along $\vec{b}$ axis.

essentially by the same three (N—H . . . Cl) hydrogen bonds as can be seen more easily in Figure 2, which represents a part of the projection of the structure along the $\vec{b}$ axis. Let us analyze the different regions of this composite structure.

b) The inorganic layer

It is built up from rows of ($CdCl_4$) tetrahedra, parallel to the a axis. Indeed, each ($CdCl_4$) tetrahedron is very distorted but possesses a mirror symmetry plane containing the Cd, Cl(3) and Cl(4) atoms. The metal atom is not located at the centre of the tetrahedra as it evidenced by the Cd—Cl(2) (2.504 Å), Cd—Cl(3) (2.600 Å) and Cd—Cl(4) (2.488 Å) bond lengths. Consequently, since the distances

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between the Cd atom and the two homologous chlorine atoms Cl(3) are equal to 2.600 Å and 2.831 Å respectively, it is possible to consider that the Cd is situated nearly in the center of a double tetrahedron with the Cl(2)-Cl(4)-Cl′(2) triangle as common face, resulting in Cl-bipyramidal chains. The large distance of 6.79 Å between two homologous chains can be considered as the consequence of the geometry of the (N—H . . . Cl) hydrogen bond scheme (Figure 2). This structural arrangement in the inorganic layer is unusual for this kind of Cd-derivative since, quite often, the mineral layer is made of corner-sharing octahedral ($CdCl_4$) forming a perovskite-type structure. Another particularly can be pointed out: it concerns the rather short bond lengths Cd—Cl′(2) = Cd—Cl(2) = 2.504 Å and Cd—Cl(4) = 2.488 Å; in "classical" perovskite-type derivatives with the cadmium as central metal atom, [12,13,14] the (Cd—Cl) bond lengths are usually close to 2.55 Å for axial chlorine atoms and 2.65 Å for equatorial chlorine atoms.

c) The organic layer

This part can be described as a double-molecular layer where the terminal (COOH) groups of the molecule in the first half-layer are connected to the corresponding ones in the second half-layer through a double carboxylic bridge. The (O—H . . . O) bond length, of 2.61 Å, is also particularly short, and it is possible to consider such a dimer as the molecular unit of the organic part of the complexe. As a consequence of the geometry of the (N—H . . . Cl) hydrogen bond scheme, the dimer is not oriented perpendicular to the inorganic layer, the angle between the long axis of the molecule and the ($CdCl_4$) layer is about 29 degrees. The shortest distance between two homologous dimers lies in the a direction and equals 5.39 Å. This value is much too large for neighbouring molecules to dimerize upon photoirradiation at room temperature. The equation of the mean plane, calculated from carbon atoms of the benzene rings is: $-0.5956\,X + 0.5196\,Y - 0.6126\,Z = 0.0098$ nm with respect to the unit-cell orthonormal axes ($Oxyz'$), z' being orthogonal to (Oxy) plane. The distances of all atoms of the organic molecule from this mean plane are given in Table VI. The oxygen atom O(28) is significantly situated out of this plane.

d) The connection between the inorganic and the organic parts through the (N—H . . . Cl) bond is strong as it can be observed from the short bond length N—H . . . Cl(2) = 3.13 Å, N—H . . . (Cl(2) + a) = 3.16 Å and N—H . . . Cl(4) = 3.14 Å. In perovskite type layer compounds, the corresponding hydrogen bonds are generally around 3.3 – 3.65 Å.[14,15,16] Owing to the two different schemes relative to the bonding between the NH_3 group and the chlorine atoms, described by Kind[2] ("orthorhombic" configuration and "monoclinic" configuration†) we can conclude that in the (4-aminocinnamic acid-$CdCl_4$ complex salt, the configuration is near to a "monoclinic" scheme since we observe two bonds with the two chlorine atoms Cl(2) situated out of the mirror plane (0,1/4,0) and one bond with a chlorine atom Cl(4) on the mirror plane.

---

†For perovskite type structures, in a "orthorhombic" configuration, two N—H . . . Cl bonds involve equatorial chlorine atomes and one N—H . . . Cl an axial whereas the "monoclinic" configuration involves two hydrogen bonds with axial chlorine atoms and one with an equatorial chlorine.

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TABLE VI

Distances of the atoms to the mean plane of the molecule

	Atom	Distances (Å)
Atoms which define the mean plane	C(11)	−0.0023 (7)
	C(12)	−0.0041 (8)
	C(13)	0.0073 (8)
	C(14)	−0.0040 (8)
	C(15)	−0.0022 (7)
	C(16)	0.0054 (7)
other atoms	N(21)	−0.0027 (7)
	C(24)	−0.0061 (8)
	C(25)	−0.2320 (9)
	C(26)	−0.1918 (9)
	O(27)	0.1224 (9)
	O(28)	−0.4695(10)

IV. THERMAL BEHAVIOUR

The thermal behaviour of the (4-aminocinnamic acid-$CdCl_4$) complex salt has been studied by powder X-ray diffraction analysis and microcalorimetry. In the first case, a Guinier-Simon camera is used in the range 100–473 K with a heating and cooling rate of 0.1 $Kmin^{-1}$, $CuK\alpha_1$ radiation and quartz monochromator. For calorimetric investigation, the experiments are performed with a Perkin-Elmer DSC-Series 7, in the range 293–503 K, and using a heating and cooling rate of 4 $Kmin^{-1}$. The results are shown on Figure 4a–4b. On the diffraction pattern (Figure 4a), no structural transformation is observed up to 450 K where all the diffraction lines disappear. This phenomenon is not due to melting since optical microscopic observations show that the tridimensional arrangement of the crystal organization is fully lost in the solid state beyond this temperature. The solid becomes somehow

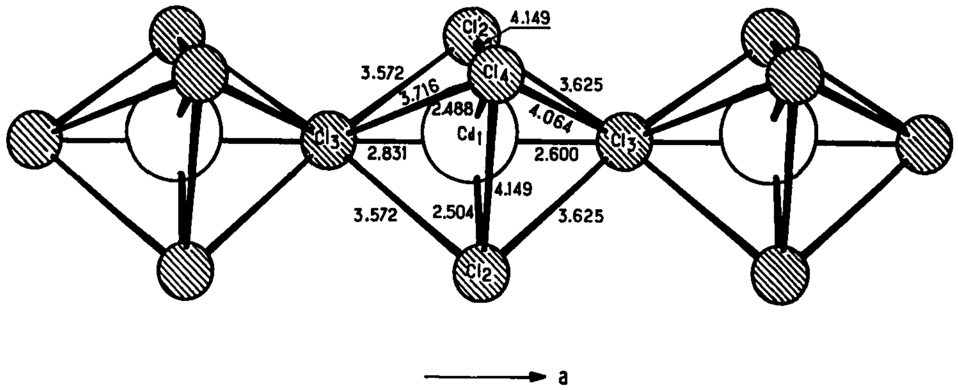

FIGURE 3 Particularities of the chains is [Cl-pyramids] of the inorganic layer.

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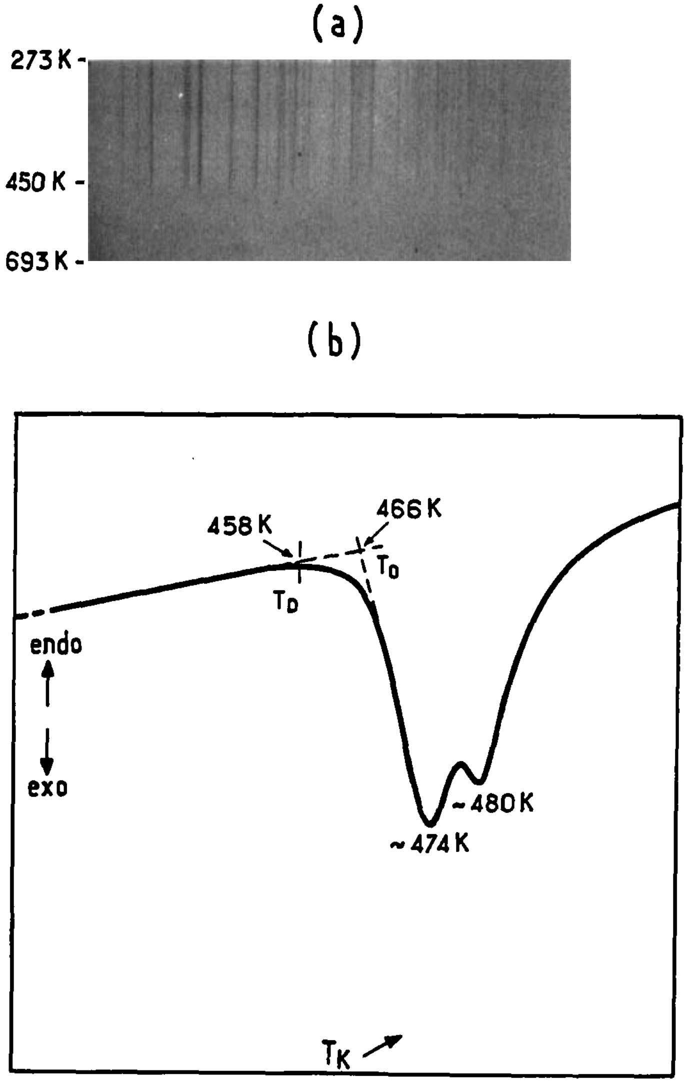

FIGURE 4 Thermal behaviour of the compound. a) Guinier Simon diffraction pattern. b) DSC experiment.

"amorphous" and this transformation is irreversible as shows the X-ray diffraction pattern corresponding to cooling procedure.

DSC investigations (Figure 4b) point out that this transformation corresponds to a large exothermic signal, stretching from 450 K to 580 K, with two maxima situated at 474 K and 480 K respectively. Here also, no calorimetric signal is observed during cooling process down to room temperature. It is possible that this exothermic phenomenon corresponds to a thermal crosslinking of (—C≡C—) units in the organic part, but further investigations with other techniques are necessary

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to consolidate this assumption. Moreover, on some first-heating DSC experiments, a small endothermic signal was detected in the range 440–450 K. Taking into account the aleatory character of the observed signal, we do not believe that it corresponds to a phase transition in the solid state since no structural change is observed at this temperature on the Guinier-Simon pattern (Figure 4a).

V. CONCLUSION

The determination of the room temperature crystal structure of the complex (4-aminocinnamic acid-$CdCl_4$) has pointed out the bidimensional structural arrangement with alternated inorganic and organic layers. The structure of the inorganic layer is unusual for Cd derivatives; it is made of chains of (Cl) bipyramids parallel to the a axis and linked to each other through the three hydrogen bonds (N—H . . . Cl) formed from the NH_3 group of the organic molecule with three chlorine atoms of the chain. Inside the organic part, two molecules of acid are bonded to each other by their (COOH) group, forming strong double carboxylate bridge.

The reasons for the photoinactivity of the compound at room temperature could be due by the too large distance ($\simeq$ 5.40 Å) between two adjacent —C=C— units, that prevents for an eventual multimerization in the organic layer. The crystalline cohesion is very high as it can be seen through the particularly short intermolecular distances in the structure. The compound is stable from 180 K to 453 K where an exothermic transformation in the solid state appears concurrently with the disappearance of the tridimensional organisation in the structure: the interpretation of this phenomenon needs further experiments, with other techniques of investigations (IR and/or NMR techniques in particular).

References

1. L. J. de Jongh and A. R. Miedena, *Adv. Phys.*, **23**, 1 (1974).
2. R. Kind, *Ferroelectrics*, **24**, 81 (1980).
3. R. Mokhlisse, M. Couzi, N. B. Chanh, Y, Haget, C. Hauw and A. Meresse, *J. Phys. Chem. Solids*, **46**, 187 (1985).
4. N. B. Chanh, C. Hauw, A. Meresse, M. Rey-Lafon and L. Ricard, *J. Phys. Chem. Solids*, **46**, 1413 (1985).
5. M. A. White, *J. Chem. Phys.*, **81**, 6100 (1984).
6. H. Hagemann and H. Bill, *J. Phys.*, **C18**, 6441 (1985).
7. B. Tieke, *Mol. Cryst. Liq. Cryst.*, **93**, 119 (1983).
8. P. Day and R. D. Ledsham, *Mol. Cryst. Liq. Cryst.*, **86**, 163 (1982).
9. B. Tieke and G. Chapuis, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 2895 (1984).
10. International Tables X-Ray Crystallography (1974). Vol. IV Birmingham; Kynoch Press (present distributor Kluwer Academic Publishers, Dordrecht).
11. R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175–3187 (1965).
12. S. Kashino, H. Oka and M. Haisa, *Acta Cryst.*, **C45**, 154–157 (1989).
13. T. Iwamoto, S. Kashino and M. Haisa, *Acta Cryst.*, **C45**, 1753–1758 (1989).
14. P. Negrier, M. Couzi, N. B. Chanh, C. Hauw and A. Meresse, *J. Phys. France*, **50**, 405–430 (1989).
15. G. Chapuis, *Acta Cryst.*, **B34**, 1506–1512 (1978).
16. R. D. Willett, *Acta Cryst.*, **B33**, 1641–1643 (1977).