

A New Investigation of Rubidium Cadmium Trichloride

F. Hamzaoui, I. Noiret, G. Odou, F. Danede, and F. Baert

Laboratoire de Dynamique et Structure des Matériaux Moléculaires, U.R.A. 801, UFR de Physique, Bât. P5, Université de Lille 1, 59655 Villeneuve D'Ascq, Cedex, France

Received September 26, 1995; in revised form February 23, 1996; accepted February 28, 1996

The structure of RbCdCl_3 has been determined from X-ray diffraction of the $\text{MoK}\alpha$ line ($\lambda = 0.7107 \text{ \AA}$) for a single crystal grown at room temperature from aqueous solution. After refinement through blocked least-squares methods, the reliability factor R in the final cycle was 3.31%, using 1955 observed reflections with $I \geq 2\sigma(I)$. The following results have been obtained, in good agreement with previous powder measurements: orthorhombic system, space group $Pnma$ (D_{2h}), $a = 8.962 \text{ \AA}$, $b = 4.034 \text{ \AA}$, $c = 14.980 \text{ \AA}$; $D_m = 3.732 \text{ g/cm}^3$, $D_x = 3.736 \text{ g/cm}^3$, $F(000) = 543.90$; $Z = 4$. Double columns of edge-sharing CdCl_6 octahedra ($\text{Cd}-\text{Cl} = 2.647 \text{ \AA}$) extending along b are linked by nine coordinated Rb ions ($\text{Rb}-\text{Cl} = 3.366 \text{ \AA}$) into a compact structure. © 1996 Academic Press, Inc.

I. INTRODUCTION

Considerable interest has recently been focused on mixed metal halides of the ABX_3 type that undergo structural transitions (1, 2). Here A = alkali metal, B = divalent metal (Pb^{2+} , Cd^{2+} , ...), and X = halogen. Many of these halides belong to the perovskite-like structure, slightly distorted by cation displacements or by tilts of BX_6 -octahedra as compared with the ideal cubic structure. The nature of the distortions is connected with the instability of lattice with respect to one or several (soft) modes vibrations.

In this paper, we report the structure of RbCdCl_3 at room temperature in order to provide better insight into the behaviour of BX_6 -octahedra in the sequence of phase transitions.

II. EXPERIMENTAL PROCEDURE

The experiments were carried out using a single crystal of RbCdCl_3 grown by slow evaporation at room temperature of an aqueous solution of RbCl and CdCl_2 in stoichiometric proportions. The compound always crystallizes in the shape of a thin rectangular parallelepiped.

A crystal with average dimensions $0.2 \times 0.15 \times 0.3 \text{ mm}$ was mounted on an Enraf-Nonius CAD-4 diffractometer with graphite-crystal monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) using an $\omega-2\theta$ scan in the range $2.65 <$

$\theta < 44.93^\circ$. A total of 2844 reflections were collected, among which only 1955 reflections, namely those for which $I \geq 2\sigma(I)$, were used to determine and refine the structure. No significant intensity variations were noticed throughout the measurements. Some reference reflections were recorded in order to control the stability of the incident beam. Accurate lattice parameters were obtained from a least-squares fit to the angular settings of 25 selective reflections. The structure was solved using direct methods with the SHELXS86 program (3, 4). The refinement was carried out using anisotropic temperature factors for the atoms (SHELX76 program) (5). The largest peaks in the final difference map were -0.69 and 1.16 e\AA^{-3} . The atomic scattering factors that correct for anomalous dispersion for Rb, Cd, and Cl and mass absorption coefficients were taken from the International Tables for X-ray Crystallography (6).

III. STRUCTURE DETERMINATION AND DISCUSSION

The compound grows at room temperature in the orthorhombic phase with four molecules per unit cell. The space group is $Pnma$ from the systematic extinctions of the reflections. The following orthorhombic lattice constants were obtained: $a = 8.962 \text{ \AA}$, $b = 4.034 \text{ \AA}$, and $c = 14.980 \text{ \AA}$ at 293 K (see Table 1). The atomic coordinates and the anisotropic displacement parameters are given in Table 2 and in Table 3 respectively. A projection of the structure along the c axis is given in Fig. 1. Our results thus seem to go against Natarajan's and Prakash's assignment of a rhombohedral form for RbCdCl_3 below 303 K (97). They also contradict Bohac *et al.* (8), who studied the $\text{RbCl}-\text{CdCl}_2$ phase diagram and then, more accurately, the different phases of RbCdCl_3 by DTA. These authors pointed out a phase transition at 387 K that they assigned to a tetragonal-cubic transition. Down to liquid nitrogen temperature they found no evidence for an orthorhombic RbCdCl_3 structure; hence they considered the tetragonal structure to be the stable room temperature phase. They suggested that water could act as an impurity that influ-

TABLE 1
Crystal Data and Structure Refinement

Empirical formula	RbCdCl ₃
Formula weight	304.22
Temperature	293 (2) K
Wavelength	0.71069 Å
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Unit cell dimensions	$a = 8.9620 (10) \text{ \AA}$ $\alpha = 90^\circ$ $b = 4.0340 (10) \text{ \AA}$ $\beta = 90^\circ$ $c = 14.9800 (20) \text{ \AA}$ $\gamma = 90^\circ$
Volume	541.6 (2) Å ³
Z	4
Density (calculated)	3.731 g/cm ³
Absorption coefficient	14.265 mm ⁻¹
F(000)	543.90
Crystal size	0.2 × 0.15 × 0.3 mm
θ range for data collection	2.65° to 44.93°
Index ranges	0 ≤ <i>h</i> ≤ 17, 0 ≤ <i>k</i> ≤ 8, 0 ≤ <i>l</i> ≤ 21
Reflections collected	1955
Independent reflections	1955 [<i>R</i> (int) = 0.0000]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Goodness-of-fit on <i>F</i> ²	1.196
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> = 0.0331

ences the polymorphism of RbCdCl₃, thus favoring the existence of an orthorhombic phase at room temperature. Without definitely refuting this idea and at this stage of the refinement it was found that adding solvent molecules (water) in the model did not change significantly the reliability factor that kept its value at 3.3%. This suggests further studies on the anhydrous RbCdCl₃ compound would be of particular interest. Our conclusion that anhydrous RbCdCl₃ is orthorhombic is in agreement with the structure found by Swanson *et al.* for the powder. A room temperature diagram for the *ABC*Cl₃ perovskites built up from the ionic radii of the *A* and *B* cations leads to the conclusion that the RbCdCl₃ compound should have a distorted orthorhombic structure under normal conditions (9).

TABLE 2
Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³)

	<i>X/A</i>	<i>Y/B</i>	<i>Z/C</i>	<i>U</i> (eq)
Cd (1)	1668 (1)	2500	558 (1)	19 (1)
Rb (1)	4274 (1)	2500	-1746 (1)	24 (1)
Cl (1)	-256 (1)	-2500	995 (1)	18 (1)
Cl (2)	3291 (1)	7500	-48 (1)	20 (1)
Cl (3)	2841 (1)	2500	2069 (1)	21 (1)

Note. Figures in parentheses are the standard error in the last decimal place quoted. *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

TABLE 3
Anisotropic Displacement Parameters (Å² × 10³)

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Cd (1)	20 (1)	18 (1)	19 (1)	0	-4 (1)	0
Rb (1)	26 (1)	22 (1)	24 (1)	0	-2 (1)	0
Cl (1)	18 (1)	21 (1)	16 (1)	0	-1 (1)	0
Cl (2)	19 (1)	17 (1)	23 (1)	0	3 (1)	0
Cl (3)	22 (1)	23 (1)	19 (1)	0	-2 (1)	0

Note. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + 2hka^*b^*U_{12}]$.

However, sometimes, after an appropriate thermal treatment, a tetragonal distorted perovskite structure can be observed at room temperature (7). In this case, RbCdCl₃ has a superstructure requiring a double cell with eight molecules per unit cell (10). Previous DTA experiments clearly brought out the metastable nature of this structure, which persists at room temperature for days before reverting to the orthorhombic form. In view of this, it is important to notice that the crystal used for our present X-ray diffraction study did not suffer any prior thermal treatment, so it was unambiguously in its orthorhombic phase.

In this orthorhombic phase, each Cd atom is surrounded by six Cl atoms that form a nearly regular octahedron (see Fig. 2). The octahedra are linked in endless chains running along the *b* axis (see Fig. 3), with two edges shared by two adjacent octahedra. A similar structure was observed and described in fuller details by Ledésert and Monier for KCdCl₃ (11). Interatomic distances and angles for RbCdCl₃ are given in Table 4.

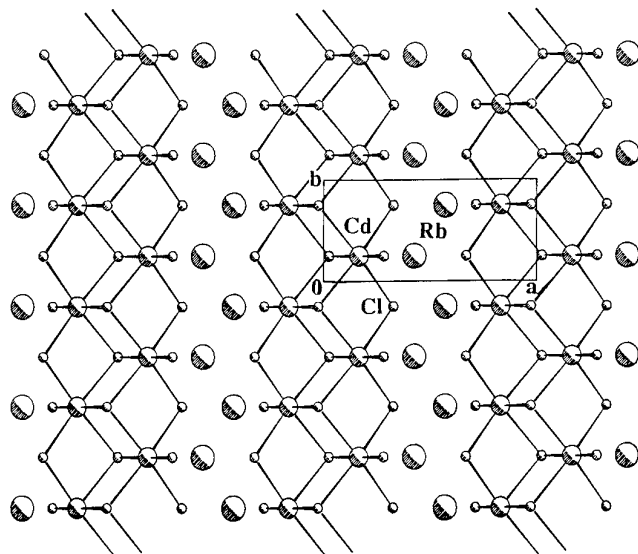


FIG. 1. Projection of the structure of RbCdCl₃ along the *c* axis.

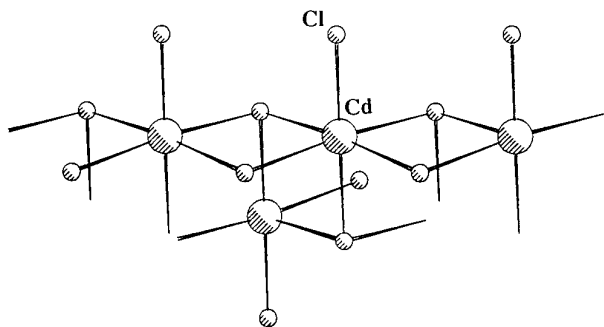


FIG. 2. Representation of the CdCl_6 octahedra.

These CdCl_6 octahedra are the cause of the phase transition observed at high temperature (7, 9). Indeed, at 413 K, a first phase transition has been observed in which a tetragonal structure has been identified. Then, at around 463 K, another phase transition has been observed in which the tetragonal phase changes to an undistorted cubic perovskite phase. Numerous papers agree about the fact that these phase transitions are caused by the condensation of a zone-boundary mode associated with the rotational vibrations of CdCl_6 octahedra (12). Figure 3 clearly exhibits a distortion of the CdCl_6 octahedra. When temperature increases these octahedra organize each other in order to reach the cubic structure.

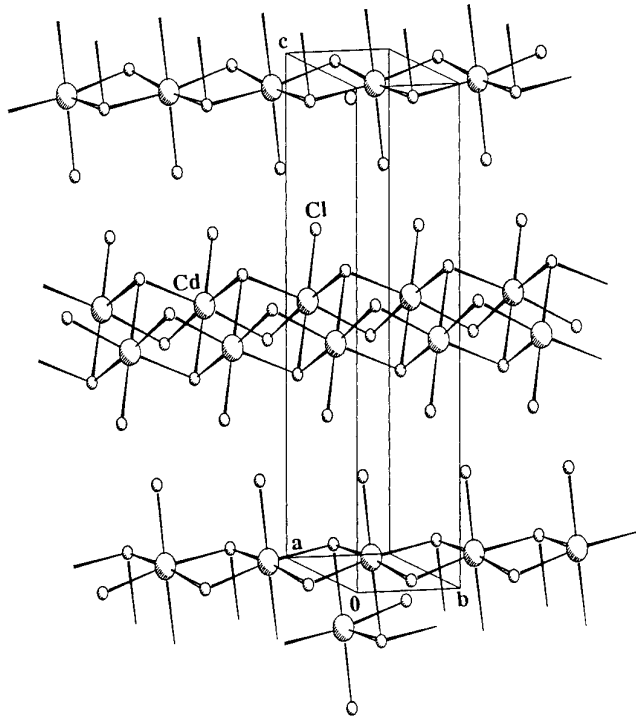


FIG. 3. Double chain of CdCl_6 octahedra built by combination of two single chains.

TABLE 4
Interatomic Distances (Å) and Angles (°)
with e.s.d.'s in Parentheses

Cd (1)–Cl (3)	2.4965 (12)
Cd (1)–Cl (2)	2.6476 (8)
Cd (1)–Cl (2) #1	2.6476 (8)
Cd (1)–Cl (1) #2	2.6478 (11)
Cd (1)–Cl (1) #3	2.7333 (9)
Cd (1)–Cl (1)	2.7333 (9)
Cd (1)–Rb (1)	4.1671 (8)
Rb (1)–Cl (2) #1	3.3633 (11)
Rb (1)–Cl (2)	3.3633 (11)
Rb (1)–Cl (1) #2	3.7722 (12)
Rb (1)–Rb (1) #1	4.0340 (10)
Rb (1)–Rb (1) #3	4.0340 (10)
Cl (1)–Cd (1) #2	2.6478 (11)
Cl (1)–Cd (1) #1	2.7333 (9)
Cl (2)–Cd (1) #3	2.6476 (8)
Cl (2)–Rb (1) #3	3.3634 (11)
Cl (3)–Cd (1)–Cl (2)	94.55 (3)
Cl (1) #3–Cd (1)–Cl (1)	95.11 (4)
Cl (3)–Cd (1)–Rb (1)	120.99 (3)
Cl (2)–Cd (1)–Rb (1)	53.70 (2)
Cl (2) #1–Cd (1)–Rb (1)	53.70 (2)
Cl (1) #2–Cd (1)–Rb (1)	62.63 (3)
Cl (1) #3–Cd (1)–Rb (1)	123.51 (2)
Cl (1)–Cd (1)–Rb (1)	123.51 (2)
Cl (2) #1–Rb (1)–Cl (1)	73.70 (3)
Cl (2) #1–Rb (1)–Cl (1) #2	61.62 (2)
Cl (2) #3–Rb (1)–Cl (1) #2	61.62 (2)

Symmetry transformations used to generate equivalent atoms: #1: $x, y - 1, z$; #2: $-x, -y, -z$; #3: $x, y + 1, z$; #4: $-x + \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$

The RbCdCl_3 crystal belongs to the $AB\text{Cl}_3$ family. Many of these compounds display a distorted structure at room temperature. A relation between the ionic radii of the ions and the stability of the crystal has been pointed out (9). In some cases the crystal goes directly from the distorted structure to the cubic structure (9), but, more frequently, it undergoes several structural phase transitions before reaching the cubic phase. The transitions are associated with rotations of the $B\text{Cl}_6$ octahedra around the principal axis. According to calorimetric measurements (7, 9), the motions of the chlorines do not seem to be independent: they move collectively so that the $B\text{Cl}_6$ octahedra remain rigid. The study of the vibrational internal modes through Raman scattering experiments would be instructive, as it should provide information about the behavior of the $B\text{Cl}_6$ octahedra and then confirm (or not) this hypothesis.

REFERENCES

1. C. J. Kroese, J. C. M. Tindemans-van-Eyndhoven, and W. J. A. Maaskant, *Solid State Commun.* **9**, 1707 (1971).

2. Y. Fujii, S. Hoshino, Y. Yamada, and G. Shirane, *Phys. Rev. B* **9**, 4549 (1974).
3. G. Germain, P. Main, and M. Woolfson, *Acta Crystallogr. Sect. A* **27**, 368 (1971).
4. G. M. Sheldrick, "Shelxs86, Program for the Solution of Crystal Structures." Univ. of Göttingen, 1986.
5. G. M. Sheldrick, "Shelxs76, Program for the Solution of Crystal Structures." Univ. of Cambridge, 1976.
6. "International Tables for X-ray Crystallography," Vol. IV, p. 149. Kynoch Press, Birmingham, 1974.
7. M. Natarajan and B. Prakash, *Phys. Status Solidi A* **4**, 167 (1971).
8. P. Bohac, A. Gaumann, and H. Arend, *Mater. Res. Bull.* **8**, 1299 (1973).
9. J. Fernandez, M. J. Tello, and M. A. Arriandiaga, *Mater. Res. Bull.* **13**, 477 (1978).
10. H. E. Swanson, H. F. McMurdie, M. C. Morris, and E. H. Evans, "Standard X-ray Diffraction Powder Patterns." Natl. Bur. Stand. (U.S.), Monogr. 25, Vol. 5, p. 43, 1967.
11. M. Ledéseret and J. C. Monier, *Acta Crystallogr. Sect. B* **40**, 73 (1984).
12. K. S. Aleksandrov, *Ferroelectrics* **20**, 61 (1978).