

## Crystal structure of $\text{RbCuCl}_3$

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### *Rubidium trichlorocuprate / Jahn-Teller effect*

**Abstract.** Rubidium trichlorocuprate,  $\text{RbCuCl}_3$ , crystallizes in the orthorhombic space group  $Pbcn$  with cell dimensions  $a = 6.98(1)$ ,  $b = 11.94(1)$ ,  $c = 6.18(1)$  Å. The diffraction pattern is only slightly perturbed from hexagonal  $P6_3/mmc$ . The structure consists of distorted centrosymmetric octahedra of chlorine atoms around each copper atom, which share faces along the  $c$ -axis to form infinite chains. Rubidium atoms lay between the polyanionic chains and together with chlorine atoms form a network, which may be regarded as distorted hexagonal closest packing of spheres. The three non-equivalent Cu–Cl bond lengths within one octahedron are 2.283, 2.398 and 2.705 Å with corresponding angles 80.0, 86.2 and 89.2°. The Cu–Cu distance is 3.09 Å.

### Introduction

The trichlorocuprate anion may appear in many different forms. Depending on the kind of the counterion, the trichlorocuprate anion exhibits a varying tendency towards polymerization, with different types of coordination around the copper(II) ion. When the cation is large, the trichlorocuprate anion usually exists in a discrete dimeric  $\text{Cu}_2\text{Cl}_6^{2-}$  form with each copper coordinated by four chlorines forming a flattened tetrahedron, with two chlorine bridges between the pair of copper atoms. When the cation is smaller, the trichlorocuprate anion becomes more polymerized with copper changing its coordination number to 5 or 6. Due to the Jahn-Teller effect, copper coordination polyhedra are usually distorted, be it flattened tetrahedra, or an elongated and skewed octahedra. Among alkaline trichlorocuprates, potassium and ammonium (Willett et al., 1963) and two forms of caesium salts (Wells, 1947; Schlueter et al., 1966; Kroese, 1974) are known, in which distorted  $\text{CuCl}_6$  octahedra share edges or faces. In the

lithium salt (Vossos et al., 1963), crystallizing with two water molecules, copper is pseudooctahedrally coordinated by five chlorines and one water molecule. Sodium trichlorocuprate and an anhydrous form of the lithium salt are not known in the crystalline state. The structure of rubidium trichlorocuprate is described in this paper.

## Experimental

Crystals of rubidium trichlorocuprate were obtained as one of two crystalline products in a reaction intended to prepare trichlorocuprate of crown-complexed rubidium. Stoichiometric amounts of copper acetate (100 mg, 0.5 mmol), rubidium carbonate (58 mg, 0.25 mmol) and dibenzo-18-crown-6 (268 mg, 1 mmol) in 50 ml of glacial acetic acid were refluxed until the solution was clear, and a few drops of concentrated hydrochloric acid were added. The colour of the reaction mixture changed from blue to green-brown. The solution was allowed to cool slowly to room temperature for several hours. The mixture of two kinds of crystals was obtained: long, well-formed dark brown-reddish needles of rubidium trichlorocuprate and very thin, badly formed brown platelets of the crown-complexed rubidium salt.

An analogous procedure applied to the caesium salt led to the formation of orange-brown needles of  $\text{CsCuCl}_3$ , of known structure (Schlueter, 1966), as the only product.

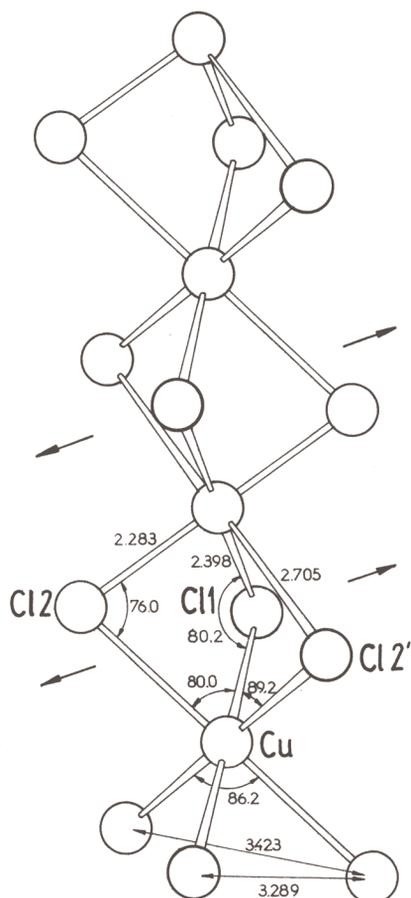
## Crystallographic data

Weissenberg photographs showed hexagonal symmetry of the crystals with systematic absences  $hh2\bar{h}l$  for  $l = 2n + 1$  and  $000l$  for  $l = 2n + 1$ , suggesting space groups  $P6_3/mmc$ ,  $P62c$  or  $P6_3mc$  with preliminary cell dimensions:  $a = 6.98$ ,  $c = 6.18$  Å. However, the accurate diffractometric measurement of  $\theta$ -values of some axial reflections revealed a small difference e.g. between reflections  $30\bar{3}0$  and  $03\bar{3}0$ . Careful inspection of non-zero layers on Weissenberg photographs confirmed that only two of the three hexagonally equivalent directions were identical and showed the presence of weak reflections which could not be indexed hexagonally. All above observations led to the orthorhombic space group  $Pbcn$ .

A crystal of dimensions  $0.13 \times 0.15 \times 0.8$  mm was mounted along its needle axis ( $c$ -direction) on a Hilger and Watts four-circle diffractometer. Accurate values of  $\theta$ -angles for 18 reflections were measured and served to calculate accurate cell dimensions from a least-squares procedure. Crystal data:  $a = 6.98(1)$ ,  $b = 11.94(1)$ ,  $c = 6.18(1)$  Å,  $V = 515$  Å<sup>3</sup>,  $D_c = 1.646$  g · cm<sup>-3</sup> for  $Z = 2$   $\text{RbCuCl}_3$  units in the unit cell,  $MW = 255.37$ ,  $F(000) = 234$ ,  $\mu = 158.1$  cm<sup>-1</sup>. The intensities were collected to a limit of  $\theta_{\max} = 57^\circ$  with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418$  Å) using  $\omega/2\theta$  scan technique. Of

**Table 1.** Atomic parameters

	<i>x</i>	<i>y</i>	<i>z</i>			
Cu	0	0	0			
Rb	0	0.3347(1)	0.25			
Cl(1)	0	0.1536(4)	0.75			
Cl(2)	0.2403(4)	0.0816(2)	0.1949(7)			
	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
Cu	0.017(2)	0.023(2)	0.057(2)	0.002(1)	-0.002(1)	-0.004(1)
Rb	0.026(2)	0.028(2)	0.093(2)	0	-0.013(1)	0
Cl(1)	0.025(3)	0.031(3)	0.099(4)	0	0.004(2)	0
Cl(2)	0.023(2)	0.026(2)	0.076(3)	-0.001(1)	-0.006(2)	-0.005(1)

**Fig. 1.** A view of  $(\text{CuCl}_3)_n$  anionic chain in  $\text{RbCuCl}_3$

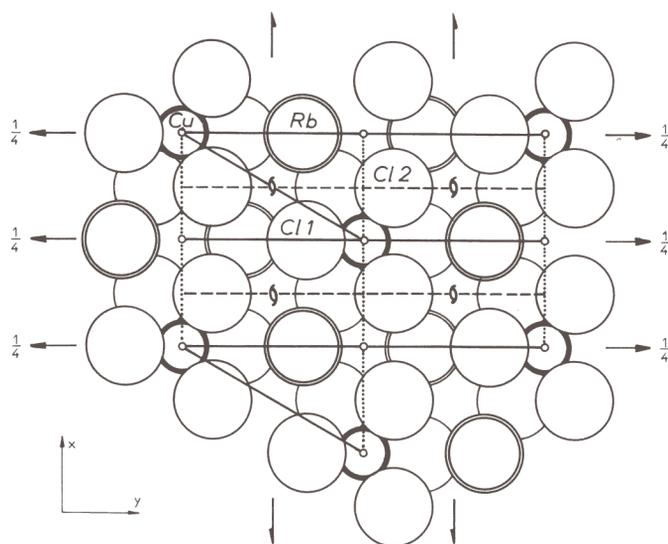


Fig. 2. The arrangement of atoms in the unit cell. The copper atoms lie at  $z=0$ , the chlorine and rubidium atoms at  $z$  about  $+\frac{1}{4}$  and  $-\frac{1}{4}$ . The pseudohexagonal cell is also shown

373 unique reflections, 65 with  $I < 2\sigma(I)$  were considered as unobserved. The intensities were corrected for Lorentz and polarization effects and empirical absorption correction based on the  $\varphi$ -dependence of the 002 reflection intensity was applied (North et al., 1968).

A comparison of the cell dimensions with those of  $\text{CsCuCl}_3$  ( $a = b = 7.216$ ,  $c = 8.178$  Å; Schlueter et al., 1966) permitted to formulate the trial model, consisting of copper atoms placed on the centre of symmetry at  $0,0,0$ , rubidium lying on the twofold axis at  $0,y,\frac{1}{4}$  with  $y = \frac{1}{3}$ , one chlorine atom occupying the special position on the twofold axis at  $0,y,\frac{3}{4}$  at the distance 2.3 Å from the copper atom, and the remaining chlorine atom in a general position at the same  $z$ -level as the previous one ( $z = \frac{3}{4}$ ) forming a triangle symmetrically placed between the two copper atoms. The model proved to be reasonable during the course of refinement. Initial value of  $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.36$  dropped quickly after a few cycles of anisotropic refinement to the final value of 0.079. The largest shift of refined parameters in the last cycle of refinement was  $0.002 \times \text{e.s.d.}$  All computations were done on a DEC-10 computer with the SHELX-76 program (Sheldrick, 1976). Atomic scattering factors were taken from International Tables, vol. IV (1974).

The final positional and thermal parameters are given in Table 1.

## Results and discussion

The copper atom, lying on the centre of symmetry at 0,0,0 is surrounded by six chlorine atoms forming distorted octahedron (Fig. 1). The three unique Cu—Cl bond distances are: Cu—Cl(1) 2.398(4), Cu—Cl(2) 2.283(4) and 2.705(4) Å with corresponding angles between them: 80.0(1), 86.2(1) and 89.2(1)°. The octahedra are stacked along the *c*-axis, sharing faces, i.e. three chlorines at about  $z = \frac{1}{4}$  belong to two coordination polyhedra, one centered on Cu at 0,0,0, another centered on Cu at 0,0, $\frac{1}{2}$ . The distance between two copper atoms is 3.09 Å, Cu—Cl—Cu' angles are 80.2 and 76.2°. Rubidium and chlorine atoms together form a network, which may be derived from hexagonal closest packing of spheres (Fig. 2). Distances between rubidium and chlorine atoms are similar to inter-chlorine contacts and are all within the range 3.28–3.77 Å. Copper atoms occupy one quarter of the octahedral voids, i.e. only those, which are formed by all six chlorine atoms.

The crystal structure of RbCuCl<sub>3</sub> exhibits close resemblance to the structure of CsCuCl<sub>3</sub> in its both known forms, low- and high-temperature stable (*P*6<sub>1</sub>22 and *P*6<sub>3</sub>*mc*, respectively). All three arrangements can be derived from h.c.p. of spheres (Cl<sup>-</sup> and Me<sup>+</sup>). In all those structures the coordination of copper ions is octahedral, distorted by Jahn-Teller effect from ideal *P*6<sub>3</sub>/*mmc* symmetry.

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