hydrogen bonds has also been observed in the crystal structures of CsH_2PO_4 (Uesu & Kobayashi, 1976) and TlH_2PO_4 (Oddon, Tranquard & Pèpe, 1979). The extended linkage of PO_4 groups through symmetrical hydrogen bonds suggests a possible ferroelectric behaviour. Because of its remarkable sensitivity to moisture, measurements of dielectric properties and pyroelectric temperature analysis (Topić, 1979) were performed on polycrystalline samples of $Pb(H_2PO_4)_2$. No determinate results could be gathered from these measurements.

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Structure of Trirubidium Heptachlorodicuprate(II)

BY W. J. CRAMA

Gorlaeus Laboratories, University of Leiden, PO Box 9502, 2300 RA Leiden, The Netherlands

Abstract. $Rb_3[Cu_2Cl_7]$, orthorhombic, *Ccca*, $T = 295$ K, $a = 24\cdot843$ (4), $b = 7\cdot216$ (1), $c = 7\cdot216$ (1) Å, $V = 1293\cdot59$ Å^3, $Z = 4$. Intensity measurements were made on a four-circle diffractometer. The final R_w value is 0·022 for 5448 reflections. The structure of this new phase in the system $RbCl–CuCl_2$ can be derived from the $Rb_3[Mn_2Cl_7]$ structure [Amit, Horowitz & Makovsky (1972). *Isr. J. Chem.* 10, 715–719]; in addition, the title compound shows a static cooperative Jahn–Teller effect. The $CuCl_6$ octahedra are elongated and order antiferrodistortively in the double layer and between similar double layers.

Introduction. In the phase diagram of RbCl and $CuCl_2$ a new compound was found in an attempt to prepare $Rb[CuCl_3]$. Because of the interest of our department in the cooperative Jahn–Teller effect, the structure of this compound could be valuable for understanding the cooperative effects in similar structure types. The related structure of $K[CuF_3]$ (Tsukuda & Okazaki, 1972) is not uniquely defined with respect to the stacking of the CuCl layers. In another related structure, $K_2[CuF_4]$ (Haegele & Babel, 1974) there seems to be a unique interaction over quite a longer distance,

but different from that found in $(NH_4)_2[CuCl_4]$ (Willett, 1964). In these compounds the Cu^{2+} ions are found in square layers together with F^- or Cl^- ions. Nearest and next-nearest interlayer interactions between the Jahn–Teller centres seem to be important. Perhaps the structure of $Rb_3[Cu_2Cl_7]$ can help to clarify the cooperative Jahn–Teller interactions between layers in this kind of structure.

By means of DTA an endothermic transition was found at 495 K. This is also the case in $Rb_2[CuCl_4]$ (495 K) (Witteveen, Jongejan & Brandwijk, 1974). This could be related to a transition to a Jahn–Teller disordered phase as described by Höck, Schröder & Thomas (1978). The compound melts/decomposes at 644 K.

Single crystals of $Rb_3[Cu_2Cl_7]$ were grown in a methyl alcohol solution. A saturated solution of RbCl in methyl alcohol was poured into a $CuCl_2$–methyl alcohol solution. The latter contains a molar excess (10%) of $CuCl_2$ and the concentration was such that no immediate crystallization occurred. Both solutions contained some ethyl orthoformate to avoid the formation of hydrates. After several hours dark-brown crystals appeared; these had a bipyramidal shape with

Table 1. *Positional parameters and equivalent isotropic thermal parameters of* Rb$_3$[Cu$_2$Cl$_7$]

		x	y	z	B_{eq} (Å^2)*
Rb(1)	4(a)	0·0	0·25	0·25	3·66 (2)
Rb(2)	8(e)	0·1796 (1)	0·25	0·25	4·13 (2)
Cu	8(e)	0·4042 (1)	0·25	0·25	2·39 (2)
Cl(1)	4(b)	0·0	0·25	0·75	3·74 (6)
Cl(2)	8(e)	0·3106 (1)	0·25	0·25	6·18 (6)
Cl(3)	16(i)	0·0930 (1)	0·0312 (1)	0·5311 (1)	3·58 (3)

* $B_{eq} = \frac{8}{3}\pi^2$ trace $\tilde{U}$.

flattened tops. Analysis for Cu gave 20·21% (theoretical: 20·12%).

The crystal symmetry of the pseudotetragonal unit cell was determined from zero- and upper-level Weissenberg photographs. Systematically absent reflections (*hkl*: $h + k = 2n + 1$, 0*kl*: $l = 2n + 1$, *h*0*l*: $l = 2n + 1$ and *hk*0: $h = 2n + 1$) show the space group to be *Ccca* (D_{2h}^{22}).

The crystal (0·18 × 0·12 × 0·13 mm) was mounted along the [100] direction on an Enraf–Nonius four-circle κ-geometry CAD-4 diffractometer with graphite-monochromated Mo *Kα* radiation. All crystallographic calculations were carried out on the Leiden University IBM 370/158 computer using a set of computer programs written or modified by Mrs Rutten-Keulemans and Dr R. A. G. de Graaff. A correction for absorbtion was made. Scattering factors and anomalous-dispersion correction factors for all ions were taken from *International Tables for X-ray Crystallography* (1974). After correction for Lorentz and polarization effects the intensities of 5448 reflections were reduced to F_o values and symmetry-related reflections were averaged.

The function minimized during the least-squares refinement process was $w_F(F_o - F_c)^2$ using the weighting scheme $w_F = 1/\sigma_F^2$ (σ_F: standard deviation of F_o). The refinement started with the transformed positions taken from the similar Rb$_3$[Mn$_2$Cl$_7$] structure. The result of the full-matrix refinement of all parameters and extinction correction in the space group *Ccca* (origin at $\bar{1}$) is given in Table 1. The final discrepancy indices are $R_w = 0·022$ and $R = 0·028$.*

A final difference Fourier synthesis had no distinct peaks larger than the standard deviation.

Discussion. In this compound the Jahn–Teller distortion of the CuCl$_6$ octahedra is clearly exhibited. The Cu–Cl distances are: Cu–Cl(1) 2·381 (1), Cu–Cl(2)

2·325 (1), Cu–Cl(3) 2·234 (1) (2×) and 2·870 (1) Å (2×). The Cu–Cl(1) and Cu–Cl(2) distances are slightly longer than one would expect in a regular D_{4h} octahedron; however, this seems to be inherent to the structure, because it occurs also in Rb$_3$[Mn$_2$Cl$_7$]. The CuCl$_6$ octahedra, which are corner-sharing, are all elongated in a direction perpendicular to the *a* axis (see Figs. 1 and 2). The cooperative effect in a layer of Cu^{2+} ions perpendicular to the *a* axis is called antiferrodistortive, since the long axes of neighbouring Cu^{2+} ions are not parallel (Höck, Schröder & Thomas, 1978). The interaction between two nearest-neighbour Cu^{2+} ions in adjacent CuCl layers (*A* and *B*) which form the double layer (see Fig. 2) is also antiferrodistortive. This part of the interaction mechanism is similar to that in K[CuF$_3$]. The Cu^{2+} ions in the *C* plane are at equal distances from four Cu^{2+} ions in the *B* plane. The direction of the long axis in the *bc* plane of
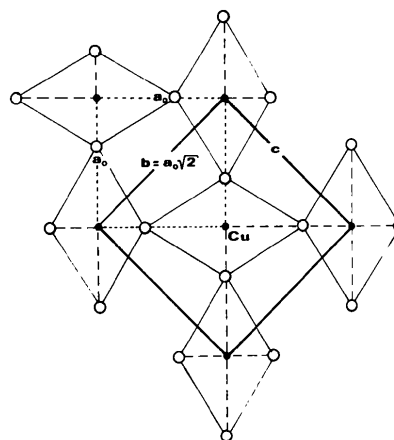

Fig. 1. CuCl plane perpendicular to the *a* axis. Open circles are Cl$^-$ ions; a_0 is the *a* axis corresponding to the Rb$_3$[Mn$_2$Cl$_7$] structure.
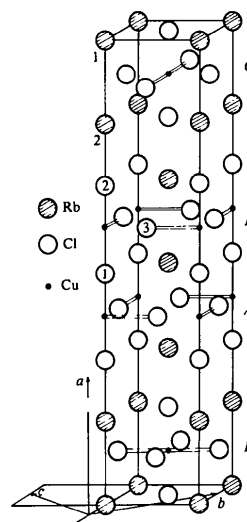
Fig. 2. Part of the unit cell of Rb$_3$[Cu$_2$Cl$_7$]. Double lines indicate a long octahedron axis.

a Cu^{2+} ion in the C plane cannot be determined by the direction of the long axes of those four Cu^{2+} ions in the B plane, because in the two possible cases this results in the same interaction mechanism (antiferrodistortive twice and ferrodistortive twice). But the interaction between layers C and D is apparently antiferrodistortive, which is similar to what has been found in $K_2[CuF_4]$.

From these results one can state that in this kind of structure type the Jahn–Teller interaction between two Cu^{2+} ions favours antiferrodistortive interactions. This implies that the long axes of the closest Jahn–Teller centres are perpendicular.

Because the shifts of the Cl^- ions in the bc plane with respect to the $Rb_3[Mn_2Cl_7]$ structure only do not result in an elongated octahedron with approximate D_{4h} symmetry, a strain should be noticed along the a axis, so that the a axis is compressed with respect to the b and c axes. Compare, therefore, the $a\sqrt{2}/b$ and c/a values, respectively for $Rb_3[Cu_2Cl_7]$: 4·88 and $Rb_3[Mn_2Cl_7]$: 5·13.

All crystals examined have the same space group and are very well crystallized. If stacking disorder is present, one should notice a seemingly large thermal movement of the $Cl(3)$ ion along the **b** and **c** directions. No evidence of disorder was found in the anisotropic temperature factors of the $Cl(3)$ ion. So it seems that

the most stable configuration in this kind of compound is an antiferrodistortive ordering between nearest layers [within the double layer (A and B)] and next-nearest layers [between the double layers (C and D)].

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Disordered Structure of Ferroelectric Ammonium Lithium Sulphate in the High-Temperature Phase

BY K. ITOH, H. ISHIKURA AND E. NAKAMURA

Faculty of Science, Hiroshima University, Hiroshima 730, Japan

Abstract. NH_4LiSO_4, $T = 478$ K, orthorhombic, *Pmcn*, $a = 5\cdot299$ (2), $b = 9\cdot199$ (2), $c = 8\cdot741$ (3) Å, $V = 426\cdot1$ Å³, $Z = 4$, $D_c = 1\cdot933$ Mg m⁻³. Residual maps displayed double-peaked contours for O atoms. The structure was refined to $R = 0\cdot055$ for 1060 observed reflexions on the basis of the split-atom method. SO_4 and LiO_4 tetrahedra lie, respectively, with equal probability in two equilibrium arrangements which have mirror symmetry with respect to each other.

Introduction. NH_4LiSO_4 undergoes two phase transitions at about 283 K (Pepinsky, Vedam, Okaya & Hoshino, 1958) and 459·7 K (Mitsui, Oka, Shiroishi,

Takashige, Iio & Sawada, 1975). The intermediate phase is ferroelectric with spontaneous polarization along the a axis (Mitsui *et al.*, 1975). The room-temperature structure was determined by Dollase (1969). We now report the crystal structure of the high-temperature phase, as part of a continuing study of the mechanism of successive phase transitions from the structural point of view.

Colourless single crystals were grown by evaporation of an aqueous solution containing equimolar amounts of $(NH_4)_2SO_4$ and $Li_2SO_4.H_2O$ at room temperature. An untwinned spherical specimen, 0·8 mm in diameter, was mounted on a Rigaku AFC-5