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Crystal Structure of $Rb_4Cu_5Cl_9$

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Crystals of $Rb_4Cu_5Cl_9$ belong to the monoclinic space group $Pa(C_s^2)$ with $a = 15.694(5)$, $b = 8.544(3)$, $c = 14.660(4)$ Å, $\beta = 106.59(2)°$ with $Z = 4$. The asymmetric unit contains 8 Rb^+, 10 Cu^+, and 18 Cl^- ions. Two of the Rb^+ ions have seven-coordination to Cl^- ions; one may be said to have (7+1)-coordination; and the remaining five have eight-coordination. One of the Cu^+ ions definitely has three-coordination to Cl^- ions; for all but one of the other nine, at least one of the Cu^+–Cl^- distances is quite long, i.e., 2.52–2.70 Å. The structure contains double chains of tetrahedral clusters of $CuCl_4$ tetrahedra along the *b*-axis. The chloride tetrahedra in each tetrahedral cluster are joined by corner sharing, forming chloride octahedra similar to those in $Rb_{18}Cu_{31}Cl_{49}$ and $Rb_4Cu_9Cl_{13}$. The clusters are joined along the *b*-axis by edge sharing with an interposed $CuCl_4$ tetrahedron. The chains are joined horizontally by corner sharing. It is shown also that Rb_2CuCl_3 is most probably isostructural with K_2CuCl_3. © 1986 Academic Press, Inc.

1. Introduction

We have pointed out elsewhere (*1*) that the system RbCl–CuCl contains four phases, apparently stable at room temperature, with formulas Rb_2CuCl_3, $Rb_4Cu_5Cl_9$, $Rb_{18}Cu_{31}Cl_{49}$, and $Rb_4Cu_9Cl_{13}$. We have reported (*1*) the crystal structure and conductivity of $Rb_{18}Cu_{31}Cl_{49}$; the results indicate that it is a true solid electrolyte, though a poor one. $Rb_4Cu_9Cl_{13}$ is a considerably better solid electrolyte than $Rb_{18}Cu_{31}Cl_{49}$, and the results of the structure analysis and conductivity measurements will be reported elsewhere (*2*).

Here we report the crystal structure of $Rb_4Cu_5Cl_9$ and also give some crystallographic data on Rb_2CuCl_3 to demonstrate that it is isostructural with K_2CuCl_3 (*3*) (see Appendix).

$Rb_4Cu_5Cl_9$ was not expected to be a solid electrolyte and electrical measurements have confirmed this: at 320°C the electrical conductivity is 10^{-7} Ω^{-1} cm^{-1}. Unlike the cases of $Rb_{18}Cu_{31}Cl_{49}$ and $Rb_4Cu_9Cl_{13}$, the structure contains no channels for movement of Cu^+ ions through it. Nevertheless, the structure has some features which are worth pointing out, especially those that support unusual aspects of the $Rb_{18}Cu_{31}Cl_{49}$ and $Rb_4Cu_9Cl_{13}$ structures.

2. Experimental

The methods of preparation of the material and of growth of crystals of $Rb_4Cu_5Cl_9$ were similar to those of $Rb_{18}Cu_{31}Cl_{49}$ (*1*) and of $Rb_4Cu_9Cl_{13}$ (*2*). The formula $Rb_4Cu_5Cl_9$ is also an unusual one; therefore, as in

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the $Rb_{18}Cu_{31}Cl_{49}$ and $Rb_4Cu_9Cl_{13}$ cases, specimens with closely neighboring formulas were made. Powder photographs supported the $Rb_4Cu_5Cl_9$ formula, later confirmed by the structure analysis.

Buerger precession camera photographs of a small crystal taken with Mo*Kα* radiation indicate that crystals of $Rb_4Cu_5Cl_9$ are monoclinic. Reflections *h*0*l* are present only when $h = 2n$, and reflections 0*k*0 are present only when $k = 2n$, implying that the most probable space group is $P2_1/a$. However, as will be seen later, the *correct* structure belongs to space group Pa.

Attempts were made to obtain spherical crystals, but only ellipsoids of revolution could be attained with a sphere grinder (*4*). The crystals have a (001) cleavage plane, probably partly the cause of the difficulty. The crystal used for data collection had a major radius of 0.11 mm and a minor radius of 0.08 mm.

The data used for the structure determination and refinement were collected with a Nicolet P3/F autodiffractometer with Mo*Kα* radiation, monochromatized by a graphite crystal. The 2θ range was 2.0–50.0°; scan speed was 2.0–29.3° per min. Scan range was from 0.8° below $K\alpha_1$ to 0.9° above $K\alpha_2$. The intensities of four reflections were checked after every 96 measurements.

Cell dimensions were determined by a least-squares fit of the setting angles of 25 reflections in a 2θ range of 10.7 to 32.4°. The results are $a = 15.694(5)$, $b = 8.544(3)$, $c = 14.660(4)$ Å, $\beta = 106.59(2)°$. The volume of the unit cell is 1884(2) Å^3. The formula weight of $Rb_4Cu_5Cl_9$ is 978.66; with four $Rb_4Cu_5Cl_9$ per unit cell, the X-ray density is 3.451 g cm^{-3}. A small single crystal sank in diiodomethane, which has a density of 3.325 g cm^{-3}.

The linear absorption coefficient for Mo*Kα* radiation is 168 cm^{-1}. Empirical absorption corrections obtained by measurement of intensities of 180 pairs of equivalent reflections were applied to the data. Lorentz-polarization corrections were also applied.

The total number of independent reflections measured was 3656, of which 1702 were accepted as observed based on the criterion:

$$F^2_{\mathrm{obs}} > 6 \cdot F_{\mathrm{obs}} \cdot \sigma(F_{\mathrm{obs}}).$$

3. Determination and Refinement of the Structure

Results of statistical calculations definitively ruled out the centrosymmetric space group, leaving Pa as most probable because the *h*0*l* class of reflections is so much larger than the 0*k*0 class. The structure was solved by direct methods (MULTAN). The peaks from MULTAN contained almost the whole structure, but the peak heights must not be taken seriously. The positions of two of the Cu^+ ions not given by MULTAN were somewhat difficult to ascertain, and in the end, it was necessary to conclude that the structure has a few anomalies.

The general, and only, positions in space group Pa are twofold: x, y, z; $x + \frac{1}{2}, \bar{y}, z$. Thus the asymmetric unit contains 36 ions: 8 Rb^+, 10 Cu^+, and 18 Cl^-. Therefore, there are 106 positional and 216 thermal parameters, a scale factor and extinction coefficient, a total of 324 parameters, to be determined and refined. The two Cu^+ ion positions that were not given by MULTAN are those of Cu6 and Cu7 (Table I). These were ascertained by difference Fourier and trial and error calculations. High thermal parameters persisted for these ions to the end.

The least-squares technique was used for refinement. Because of numerous high pair correlations, some as high as ±0.95, there were some oscillations in parameters. However, in the final cycles all 324 parameters were allowed to vary and for the very last one, the ratios |parameter shift/standard error| were between 0.0 and 0.27 and 161 were less than 0.10, indicating effective convergence. For the 1702 observed reflections, $R = \Sigma||F_{obs}| - |F_{calc}||/\Sigma|F_{obs}| = 0.034$.[1] The final estimated standard error of an observation of unit weight is 0.99. The value of the extinction coefficient, g, which the program applies to the F_{calc} as

$$|F_c|(1 + gI_c)^{-1},$$

converged to 6.326×10^{-7}; I_c is the calculated intensity.

The final results of the refinement are given in Tables I–III: Table I, positional parameters and the equivalent isotropic thermal parameters, B_{eq}; Table II, thermal parameters, $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$; Table III, the axial lengths of the root mean square vibration ellipsoids.

Calculations were also done on the enantiomorph; they could not distinguish between the two; that is, the R-values were the same. Some minor differences outside 3σ limits occurred; these also did not indicate which was the more likely. The comparison of individual $|F_{calc}|$ vs $|F_{obs}|$ pairs also did not give an indication.

The calculations were carried out with the Structure Determination Package on the PDP11/23 supplied by Molecular Structure Corporation, modified for ions. Atomic scattering factors were taken from Volume 4 of the International Tables for Cystallography.

TABLE I

POSITIONAL PARAMETERS AND B_{eq}

Atom	x	y	z	B_{eq} (Å^2)
Rb1	0.000	0.3344(3)	0.000	3.59(5)
Rb2	0.2967(1)	0.1561(3)	0.0135(2)	4.21(6)
Rb3	0.4792(1)	0.4860(3)	−0.4699(2)	3.35(5)
Rb4	0.1103(1)	0.0185(3)	−0.4783(2)	3.63(5)
Rb5	−0.1194(1)	0.1648(3)	0.2655(2)	3.55(5)
Rb6	−0.4180(1)	0.3410(3)	0.2540(2)	3.68(5)
Rb7	−0.2334(1)	0.4825(3)	−0.2544(2)	4.23(5)
Rb8	−0.6021(1)	0.0168(3)	−0.2620(2)	3.84(5)
Cu1	−0.2852(2)	−0.3982(5)	0.4450(2)	5.53(9)
Cu2	−0.1661(2)	−0.1119(4)	0.4429(2)	4.30(7)
Cu3	−0.4557(2)	0.3782(5)	−0.1696(3)	6.04(9)
Cu4	−0.3310(2)	0.0990(4)	−0.1729(3)	5.36(9)
Cu5	−0.1730(2)	−0.3737(4)	0.2500(2)	4.35(7)
Cu6	0.1201(2)	0.1054(5)	0.2248(3)	9.2(1)
Cu7	−0.2449(3)	0.3642(6)	0.0227(4)	9.5(1)
Cu8	−0.4438(2)	0.1512(5)	0.0094(3)	7.7(1)
Cu9	−0.2127(2)	0.2447(4)	0.4803(3)	4.68(8)
Cu10	−0.4095(2)	−0.2570(4)	−0.2153(3)	5.20(8)
Cl1	−0.3227(4)	0.3448(9)	−0.4693(4)	4.5(1)
Cl2	−0.0816(3)	0.1300(8)	−0.4779(5)	3.8(1)
Cl3	−0.1953(3)	0.1745(8)	−0.0998(5)	4.2(1)
Cl4	0.4498(3)	0.2974(7)	−0.0821(4)	3.8(1)
Cl5	−0.3135(4)	−0.2904(8)	0.1654(4)	4.6(2)
Cl6	−0.3085(4)	0.2076(9)	0.1102(4)	5.4(2)
Cl7	−0.5062(3)	0.0015(7)	0.1349(4)	3.3(1)
Cl8	−0.1139(4)	0.4979(8)	0.1369(4)	4.1(1)
Cl9	−0.2906(3)	0.0342(7)	0.3541(4)	3.3(1)
Cl10	−0.2083(3)	0.4470(9)	0.3615(4)	4.1(1)
Cl11	−0.4303(4)	−0.3182(7)	0.3712(5)	4.0(1)
Cl12	−0.0703(4)	−0.1943(7)	0.3607(4)	3.3(1)
Cl13	−0.3024(3)	−0.1587(7)	−0.2637(4)	3.7(1)
Cl14	0.4608(3)	−0.3732(7)	−0.2616(4)	3.0(1)
Cl15	−0.3317(3)	−0.4709(7)	−0.0826(4)	3.5(1)
Cl16	−0.4165(3)	−0.0521(5)	−0.0904(3)	2.29(9)
Cl17	−0.4327(3)	0.2372(7)	−0.2929(3)	2.7(1)
Cl18	−0.1901(4)	−0.2650(8)	−0.4413(5)	4.4(1)

Note. For this case, $B_{eq} = \frac{4}{3} * \{a^2 * \beta(1,1) + b^2 * \beta(2,2) + c^2 * \beta(3,3) + 2 * a * c * \beta(1,3) * \cos\beta\}$.

4. Description of the Structure

A projection of the structure down the b-axis is shown in Fig. 1; a stereographic pair, looking almost along the b-axis is given in Fig. 2.

The Rb^+ ion coordination in this struc-

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[1] See NAPS document No. 04374 for 12 pages of supplementary material. Order from ASIS/NAPS, Micofiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

TABLE II

GENERAL TEMPERATURE FACTOR EXPRESSIONS—*U*'S

Name	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$	U_{iso}
Rb1	0.048(1)	0.037(1)	0.050(1)	−0.010(1)	0.0111(9)	−0.006(1)	0.045(1)
Rb2	0.034(1)	0.052(1)	0.065(2)	0.006(1)	0.001(1)	0.010(1)	0.053(1)
Rb3	0.042(1)	0.044(1)	0.037(1)	0.018(1)	0.0041(9)	0.013(1)	0.042(1)
Rb4	0.045(1)	0.041(1)	0.049(1)	0.005(1)	0.0085(9)	−0.010(1)	0.046(1)
Rb5	0.0414(8)	0.056(1)	0.043(1)	0.020(1)	0.0217(7)	0.008(1)	0.045(1)
Rb6	0.052(1)	0.042(1)	0.047(1)	−0.001(1)	0.0162(9)	−0.019(1)	0.047(1)
Rb7	0.061(1)	0.051(1)	0.059(1)	0.019(1)	0.0326(9)	0.013(1)	0.054(1)
Rb8	0.044(1)	0.049(1)	0.057(1)	−0.008(1)	0.0199(8)	−0.007(1)	0.049(1)
Cu1	0.039(1)	0.090(2)	0.075(2)	0.002(2)	0.005(1)	−0.049(2)	0.070(1)
Cu2	0.064(1)	0.043(2)	0.064(2)	0.005(1)	0.030(1)	0.018(2)	0.054(1)
Cu3	0.084(2)	0.087(3)	0.073(2)	−0.024(2)	0.046(1)	−0.020(2)	0.076(1)
Cu4	0.047(2)	0.061(2)	0.080(2)	−0.005(2)	−0.007(2)	0.007(2)	0.068(1)
Cu5	0.063(1)	0.061(2)	0.050(2)	0.021(1)	0.031(1)	0.017(2)	0.055(1)
Cu6	0.048(2)	0.141(3)	0.116(3)	−0.063(2)	−0.047(2)	0.081(2)	0.117(1)
Cu7	0.108(2)	0.132(3)	0.132(3)	0.042(3)	0.053(2)	0.092(2)	0.120(1)
Cu8	0.059(2)	0.109(3)	0.097(3)	0.039(2)	−0.025(2)	−0.045(2)	0.096(1)
Cu9	0.034(1)	0.064(2)	0.087(2)	−0.002(1)	0.028(1)	−0.008(2)	0.059(1)
Cu10	0.066(2)	0.052(2)	0.088(2)	−0.016(1)	0.035(1)	−0.021(2)	0.066(1)
Cl1	0.067(3)	0.063(4)	0.048(3)	0.003(3)	0.027(2)	−0.015(3)	0.057(1)
Cl2	0.025(2)	0.053(4)	0.061(4)	−0.006(2)	0.003(2)	−0.015(3)	0.048(1)
Cl3	0.022(2)	0.074(4)	0.060(4)	−0.001(3)	0.008(2)	0.003(4)	0.053(1)
Cl4	0.038(2)	0.059(4)	0.057(3)	0.008(2)	0.030(2)	0.024(3)	0.048(1)
Cl5	0.038(3)	0.081(5)	0.037(3)	0.013(3)	−0.018(3)	−0.010(3)	0.058(1)
Cl6	0.071(3)	0.093(5)	0.053(3)	−0.047(3)	0.040(2)	−0.005(3)	0.068(1)
Cl7	0.019(2)	0.044(3)	0.059(3)	−0.012(2)	0.005(2)	−0.016(3)	0.042(1)
Cl8	0.066(3)	0.067(4)	0.028(2)	−0.016(3)	0.025(2)	−0.019(3)	0.052(1)
Cl9	0.061(3)	0.035(3)	0.026(2)	−0.010(2)	0.010(2)	0.016(2)	0.042(1)
Cl10	0.039(3)	0.078(4)	0.033(3)	−0.002(3)	0.001(2)	0.012(3)	0.052(1)
Cl11	0.054(3)	0.029(3)	0.067(4)	0.013(2)	0.010(3)	−0.020(3)	0.051(1)
Cl12	0.059(3)	0.025(3)	0.040(3)	0.006(2)	0.010(2)	0.009(3)	0.042(1)
Cl13	0.036(2)	0.037(3)	0.082(3)	0.003(2)	0.040(2)	−0.004(3)	0.047(1)
Cl14	0.057(3)	0.032(3)	0.029(3)	−0.008(2)	0.016(2)	−0.010(2)	0.038(1)
Cl15	0.023(2)	0.053(3)	0.053(3)	−0.008(2)	0.003(2)	0.023(3)	0.044(1)
Cl16	0.048(2)	0.008(2)	0.041(2)	0.004(2)	0.028(2)	0.009(2)	0.029(1)
Cl17	0.038(2)	0.051(3)	0.009(2)	0.020(2)	0.001(2)	0.001(2)	0.034(1)
Cl18	0.058(3)	0.037(3)	0.075(4)	0.007(3)	0.028(2)	−0.013(3)	0.056(1)

Note. $U_{iso} = B_{eq}/8\pi^2$.

ture is between that of Rb_2CuCl_3 and $Rb_{18}Cu_{31}Cl_{49}$ (*1*). In Rb_2CuCl_3 which we believe to be isostructural with K_2CuCl_3 (see Appendix), the coordination number (C.N.) must be seven, whereas in $Rb_{18}Cu_{31}Cl_{49}$ it is nine for one Rb^+ ion and what has been called (7 + 2) for the other. In $Rb_4Cu_5Cl_9$ (Table IV, Figs. 1 and 2), at least two of the Rb^+ ions, Rb2 and 6, have C.N. 7; at least four, Rb 3, 4, 5, and 8, appear to have C.N. 8. Rb1 has seven Cl^- neighbors at distances 3.21–3.50 Å with an average of 3.34 Å, which is a good C.N. 7 distance for Rb^+–Cl^- (*1*). If the longer distance, 3.72 Å, is included, the average Rb^+–Cl^- distance becomes 3.39 Å, which is in good agreement with the C.N. 8 Rb^+–Cl^- distance of 3.38 Å. Rb7 has five Rb–Cl distances at 3.22–

TABLE III

ROOT MEAN SQUARE AMPLITUDES OF THERMAL VIBRATION IN ÅNGSTROMS

Atom	Min.	Intermediate	Max.
Rb1	0.174	0.228	0.233
Rb2	0.170	0.231	0.279
Rb3	0.138	0.218	0.247
Rb4	0.181	0.207	0.250
Rb5	0.153	0.200	0.268
Rb6	0.156	0.227	0.253
Rb7	0.188	0.203	0.290
Rb8	0.191	0.216	0.250
Cu1	0.180	0.200	0.371
Cu2	0.176	0.231	0.281
Cu3	0.211	0.254	0.347
Cu4	0.197	0.244	0.325
Cu5	0.184	0.203	0.301
Cu6	0.121	0.217	0.537
Cu7	0.198	0.304	0.477
Cu8	0.185	0.243	0.448
Cu9	0.164	0.249	0.299
Cu10	0.200	0.236	0.319
Cl1	0.176	0.262	0.269
Cl2	0.149	0.217	0.275
Cl3	0.148	0.248	0.273
Cl4	0.138	0.200	0.291
Cl5	0.123	0.246	0.313
Cl6	0.119	0.242	0.362
Cl7	0.117	0.204	0.264
Cl8	0.128	0.226	0.294
Cl9	0.105	0.207	0.265
Cl10	0.165	0.214	0.287
Cl11	0.122	0.229	0.294
Cl12	0.143	0.211	0.249
Cl13	0.126	0.195	0.294
Cl14	0.141	0.189	0.244
Cl15	0.142	0.175	0.287
Cl16	0.073	0.154	0.240
Cl17	0.095	0.159	0.259
Cl18	0.164	0.243	0.283

TABLE IV

Rb–Cl DISTANCES AND STANDARD ERRORS (Å)

Site	Rb–Cl				Av.
Rb1	Cl3	3.29(1)	Cl8	3.35(1)	
	Cl4	3.38(2)	Cl14	3.72(1)	
	Cl5	3.25(1)	Cl15	3.41(1)	3.34(1)
	Cl7	3.50(2)	Cl16	3.21(1)	(3.39)
Rb2	Cl3	3.30(2)	Cl8	3.54(2)	
	Cl4	3.33(1)	Cl15	3.42(1)	
	Cl5	3.39(2)	Cl16	3.38(1)	3.39(1)
	Cl7	3.37(1)			
Rb3	Cl1	3.33(1)	Cl12	3.45(1)	
	Cl2	3.41(2)	Cl14	3.37(1)	
	Cl10	3.31(1)	Cl17	3.34(1)	3.38(1)
	Cl11	3.48(2)	Cl18	3.38(1)	
Rb4	Cl1	3.27(1)	Cl12	3.62(2)	
	Cl2	3.16(1)	Cl13	3.28(2)	
	Cl9	3.29(1)	Cl17	3.70(1)	3.41(1)
	Cl11	3.32(1)	Cl18	3.68(1)	
Rb5	Cl2	3.65(2)	Cl9	3.48(1)	
	Cl6	3.20(2)	Cl10	3.30(2)	
	Cl7	3.28(1)	Cl11	3.21(1)	3.37(1)
	Cl8	3.43(2)	Cl12	3.37(1)	
Rb6	Cl6	3.28(2)	Cl10	3.34(1)	
	Cl7	3.46(1)	Cl11	3.41(1)	
	Cl8	3.36(1)	Cl12	3.44(1)	3.38(1)
	Cl9	3.37(1)			
Rb7	Cl1	3.28(2)	Cl14	3.22(1)	
	Cl3	3.41(2)	Cl15	3.33(1)	
	Cl4	3.75(2)	Cl17	3.67(1)	3.41(1)
	Cl13	3.24(1)	Cl18	3.70(1)	(3.45)
Rb8	Cl2	3.50(2)	Cl14	3.48(1)	
	Cl3	3.53(2)	Cl16	3.31(1)	
	Cl4	3.49(2)	Cl17	3.39(1)	3.42(1)
	Cl13	3.36(1)	Cl18	3.35(2)	

3.41 Å, two at 3.67 and 3.70 Å, and one at 3.75 Å. The first seven average 3.41 Å, which is 0.03 Å greater than a C.N. 7 distance; if the longest distance is included, the average is 3.45 Å, which is rather long for the C.N.-8 distance. Perhaps in analogy with the so-called (7+2)-coordination, this could be called (7+1).

RbCl has the NaCl structure; therefore, the Rb^+ ion is coordinated to six Cl^- ions. In $Rb_4Cu_9Cl_{13}$, all the Rb^+ ions have C.N. 9. Thus, there is an interesting trend in the structures of the RbCl–CuCl system. The coordination of the Rb^+ to Cl^- ions increases with the Cl^-/Rb^+ ratio and decreases with the Cl^-/Cu^+ ratio. This should not be surprising; however, such trends do not always occur. For example, in both CsCl and $CsCu_2Cl_3$ (5), the Cs^+ ion has C.N. 8.

Tetrahedral clusters of $CuCl_4$ tetrahedra

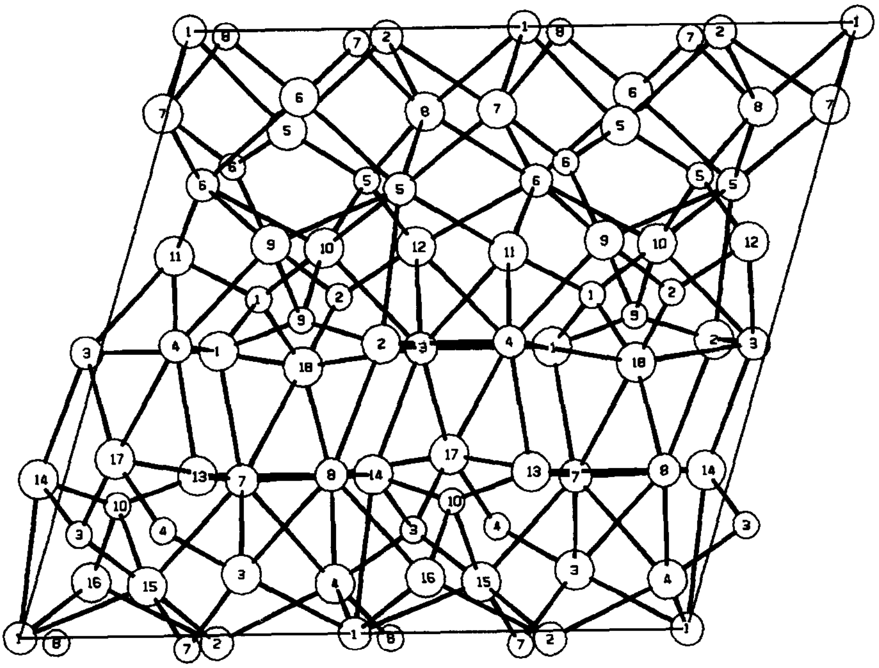

FIG. 1. Projection of the structure down the *b*-axis. The smallest circles represent Cu^+ ions, the intermediate circles, Rb^+ ions, and the largest, Cl^- ions.

are joined into rather complicated double chains that are parallel to the *b*-axis (Fig. 3). The periodicity of these chains, along the *b* axis, is easily seen in Fig. 3. The double chains are isolated from each other in the *a* and *c* directions by intervening Rb^+ ions.

Two tetrahedral groups of Cu^+ ions (Fig. 3) are formed by Cu 1, 2, 5, 6 in the left

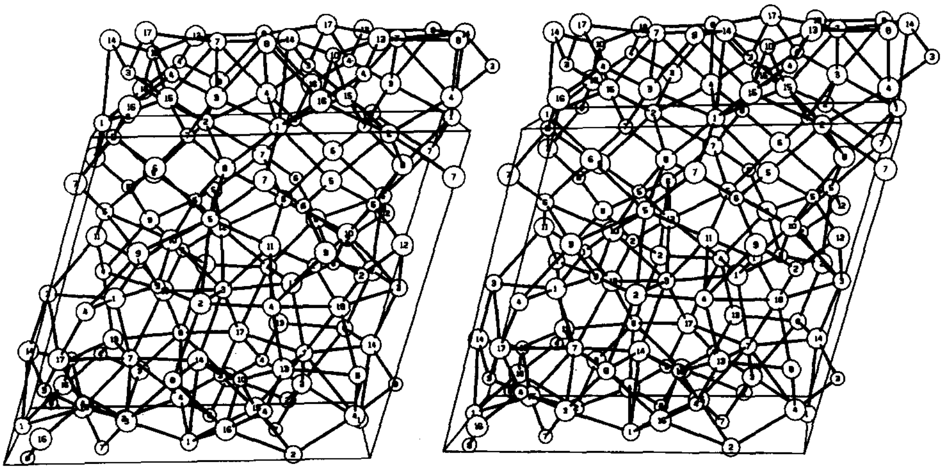

FIG. 2. Stereoscopic view of the structure roughly down the *b*-axis. The smallest circles represent Cu^+ ions, the intermediate circles, Rb^+ ions, and the largest, Cl^- ions.

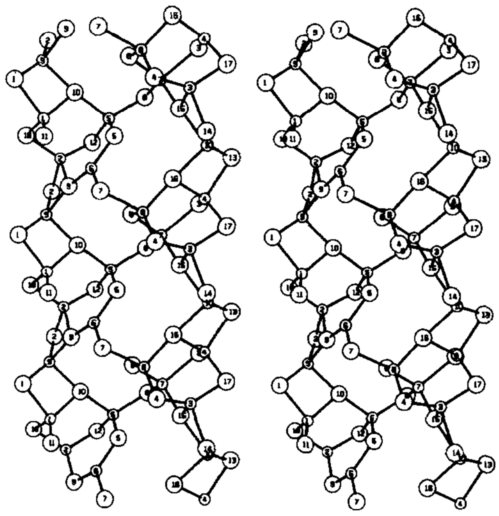

FIG. 3. Stereoscopic view of the chains of $CuCl_4$ tetrahedra.

chain of Fig. 3 and by Cu 3, 4, 7, 8 in the right chain. The chloride tetrahedra of each tetrahedral group of Cu^+ ions are joined by corner sharing, thereby forming chloride octahedra, similar to those in $Rb_{18}Cu_{31}Cl_{49}$ and $Rb_4Cu_9Cl_{13}$. In the chain on the left the tetrahedral cluster is joined to the next one along *b* by edge sharing with the interposed Cu9 tetrahedron of chlorides (Fig. 3). On the right, the joining is made by edge sharing with the interposed Cu10 tetrahedron of chlorides. The two chains are joined horizontally by corner sharing, that is, of Cl7 and Cl8 (Fig. 3).

In CuCl, each Cu^+ ion is surrounded by a regular tetrahedron of Cl^- ions, with Cu–Cl distance, 2.345 Å, and Cl–Cl distance, 3.830 Å. The average Cu–Cl values (Table V) for Cu4, 5, 7, and 10 are significantly higher than the average Cu–Cl distance in CuCl. In Ref. (*1*), we have considered a tetrahedral Cu–Cl distance greater than or equal to 2.64 Å as "very long" and one equal to 2.52 Å as "rather long." In $Rb_4Cu_5Cl_9$, all the Cu^+ ions but Cu5, have at least one very long or one rather long Cu–Cl dis-

TABLE V

INTERIONIC DISTANCES (Å) OF THE Cu–Cl TETRAHEDRA

Site	Cu–Cl (Å)				Av Cu–Cl (Å)	Cl–Cl[b] (Å)						Av Cl–Cl (Å)
Cu1	Cl1	2.68(2)	Cl11	2.33(2)		Cl1–Cl10	3.56	Cl1–Cl18	3.89	Cl10–Cl18	3.75	
	Cl10	2.36(2)	Cl18	2.21(2)	2.40(2)	Cl1–Cl11	3.79	Cl10–Cl11	4.06	Cl11–Cl18	4.01	3.84
Cu2	Cl2	2.55(2)	Cl12	2.29(2)		Cl2–Cl9	3.59	Cl2–Cl18	3.89	Cl9–Cl18	3.91	
	Cl9	2.37(1)	Cl18	2.26(2)	2.37(2)	Cl2–Cl12	3.68	Cl9–Cl12	3.95	Cl12–Cl18	3.93	3.83
Cu3	Cl4	2.33(1)	Cl15	2.38(2)		Cl4–Cl14	3.89	Cl4–Cl17	4.06	Cl14–Cl17	3.81	
	Cl14	2.65(2)	Cl17	2.29(1)	2.41(2)	Cl4–Cl15	3.96	Cl14–Cl15	3.65	Cl15–Cl17	3.93	3.88
Cu4	Cl3	2.19(1)	Cl16	2.42(1)		Cl3–Cl13	3.79	Cl3–Cl17	4.02	Cl13–Cl17	3.91	
	Cl13	2.68(2)	Cl17	2.33(1)	2.41(1)	Cl3–Cl16	4.01	Cl13–Cl16	3.62	Cl16–Cl17	3.82	3.86
Cu5	Cl5	2.31(1)	Cl10	2.42(2)		Cl5–Cl8	3.74	Cl5–Cl12	4.15	Cl8–Cl12	4.11	
	Cl8	2.39(1)	Cl12	2.47(2)	2.40(1)	Cl5–Cl10	3.65	Cl8–Cl10	4.00	Cl10–Cl12	3.75	3.90
Cu6	Cl5	2.21(2)	Cl9	2.34(1)	2.26(1)	Cl5–Cl7	3.85	Cl7–Cl9	3.96			3.89
	Cl7	2.24(1)	Cl11	3.08(2)[a]		Cl5–Cl9	3.86					
Cu7	Cl3	2.70(2)	Cl8	2.52(2)		Cl3–Cl6	3.98	Cl3–Cl15	3.76	Cl6–Cl15	3.88	
	Cl6	2.27(2)	Cl15	2.24(2)	2.43(2)	Cl3–Cl8	4.33	Cl6–Cl8	3.87	Cl8–Cl15	3.98	3.97
Cu8	Cl4	2.21(2)	Cl7	2.65(2)		Cl4–Cl6	4.10	Cl4–Cl16	3.67	Cl6–Cl16	3.69	
	Cl6	2.27(2)	Cl16	2.39(1)	2.38(2)	Cl4–Cl7	3.85	Cl6–Cl7	3.67	Cl7–Cl16	3.97	3.85
Cu9	Cl1	2.23(2)	Cl9	2.62(2)		Cl1–Cl2	4.24	Cl1–Cl10	3.56	Cl2–Cl10	3.76	
	Cl2	2.20(2)	Cl10	2.47(2)	2.38(2)	Cl1–Cl9	3.84	Cl2–Cl9	3.59	Cl9–Cl10	3.75	3.79
Cu10	Cl13	2.17(1)	Cl15	2.70(2)		Cl13–Cl14	4.15	Cl13–Cl16	3.62	Cl14–Cl16	3.84	
	Cl14	2.19(2)	Cl16	2.56(2)	2.41(2)	Cl13–Cl15	3.88	Cl14–Cl15	3.65	Cl15–Cl16	3.81	3.82

[a] Considered to be nonbonding.
[b] All standard errors are 0.02 Å.

TABLE VI

DISTANCE OF Cu^+ ION TO NEAREST Cl PLANE AND RMS VIBRATION AMPLITUDE AND Cu–Cl BOND IN SAME DIRECTION

Cu^+ ion number	Nearest Cl plane	Distance (Å) Cu to plane	$\langle U_\perp \rangle$ (Å)	Bond direction
1	10, 11, 18	0.32	0.37	Cu1–Cl1
2	9, 12, 18	0.40	0.27	Cu2–Cl2
3	4, 15, 17	0.37	0.34	Cu3–Cl14
4	3, 16, 17	0.34	0.30	Cu4–Cl13
5	5, 8, 12	0.59	0.21	Cu5–Cl10
6	5, 7, 9	0.26	0.54	Cu6–Cl11
7	6, 8, 15	0.63	0.40	Cu7–Cl3
8	4, 6, 16	0.51	0.45	Cu8–Cl7
9	1, 2, 10	0.34	0.25	Cu9–Cl9
10	13, 14, 16	0.35	0.30	Cu10–Cl15

Note. $\langle U_\perp \rangle$ is the rms vibration amplitude perpendicular to the plane.

tance associated with them. The Cu6–Cl11 distance, 3.08 Å, is so long that Cl11 should not be considered to be coordinated to Cu6. Thus Cu6 has three-coordination, with average Cu–Cl distance, 2.26 Å (Table V). The Cu6 ion does not lie in the plane of Cl5, 7, and 9, to which Cl6 is coordinated; its distance from the plane is 0.26 Å. The Cu6 ion has large thermal vibrations (Tables I–III); its maximum vibration amplitude, 0.54 Å is in a direction perpendicular to the Cl5, 7, 9 plane, which is also close to the Cu6–Cl11 direction. It is clear, that in this direction, thermal vibration of the Cu6 ion carries it to a distance of 0.28 Å on the other side of the Cl5, 7, 9 plane. It should be noted (Figs. 2 and 3) that the direction of the maximum amplitude of vibration of the Cu6 ion is *not* into the "included" Cl octahedron.

In CuCl, the distance of the Cu^+ ion to the faces of the Cl tetrahedron is 0.78 Å ($a/4\sqrt{3}$). For five of the nine Cu^+ ions in Cl tetrahedra in $Rb_4Cu_5Cl_9$, the distance (Table VI) of the Cu^+ ion to the nearest Cl plane in the tetrahedron is less than half 0.79 Å. For all the Cu^+ ions but Cu5, the rms vibration amplitude in the direction of this distance is very close to the maximum (Tables III and VI). Furthermore, except for Cu5, these are very nearly along the longest Cu–Cl distances. Cu5 does not have a particularly long Cu–Cl distance (Table V) relative to its average Cu–Cl distance.

Of the eight Cu^+ ions that are in the two tetrahedral clusters and, except for Cu6, have Cl tetrahedra that share a face with an empty octahedron, the high rms vibration amplitudes of Cu1, 2, 3, 4, 8 of Table VI are perpendicular to the octahedral faces. The Cl6, 8, 15 face of the Cu7 tetrahedron is shared with an empty Cl *tetrahedron* formed by Cl5, 6, 8, 15 (Figs. 2 and 3). The face that the Cu5 tetrahedron shares with one of the empty chloride octahedra is formed by Cl5, 10, 12 (Fig. 3); the Cu5 ion is 0.87 Å from this plane and the rms vibration amplitude in this direction is 0.20 Å. The face shared by the Cu7 tetrahedron and the other empty octahedron is formed by Cl3, 8, 15 (Fig. 3); the Cu7 ion is 0.87 Å from this plane and the rms vibration amplitude in this direction is 0.26 Å.

The tetrahedral clusters of Cu^+ ions may be compared with the tetrahedral arrangement of Cu^+ ions in zinc blende-type CuCl in which each Cu^+–Cu^+ distance is 3.830 Å equal to the Cl^-–Cl^- distance. In the Cu1, 2, 5, 6 cluster (Fig. 3), the distances (omitting the Cu prefix) are: 1–2, 3.09(1); 1–5, 3.77(1); 1–6, 4.02(1); 2–5, 3.58(1); 2–6, 3.92(1); 5–6, 3.906(8) Å. The average value is 3.71(1) Å. In the Cu3, 4, 7, 8 cluster (Fig. 3), the distances are: 3–4, 3.10(1); 3–7, 3.69(1); 3–8, 3.23(1); 4–7, 3.60(2); 4–8, 3.63(1); 7–8, 3.57(1) Å. The average value is 3.47(1) Å. Most of these Cu–Cu distances are significantly shorter than the Cu–Cu distance in CuCl. This result is a consequence of the short distances between the Cu^+ ions and the faces shared with the empty octahedra.

The three structures, i.e., of $Rb_4Cu_5Cl_9$, $Rb_{18}Cu_{31}Cl_{49}$(1), and $Rb_4Cu_9Cl_{13}$(2) show, at the very least, a *tendency* of the Cu^+ ion toward three-coordination, supporting the suggestion (*6*) that the Cu^+ ion is favorable to ionic conductivity in solids because it is stable in both tetrahedral and three-coordination.

The plane $z \cong 0.59$ cuts only Rb^+–Cl^- bonds (Fig. 1). The bonding across this plane is weak enough to allow the crystals to cleave in it; i.e., the (001) plane is a cleavage plane. A similar cleavage plane occurs in $CsCu_2Cl_2I$ (*5*).

It has been pointed out earlier that reflections $0k0$ are absent when k is odd, but also that the structure does not contain any 2_1 axes. This can be readily explained by referring to the coordinates of the equipoints in *Pa*, namely (x, y, z) and $(\frac{1}{2} + x, \bar{y}, z)$ and to Table I: it is seen that the y coordinates of pairs of ions (1–2; 3–4, etc.) in the table are related closely by $y, \frac{1}{2} + y$, if one takes the proper sign for y in each case. For example, taking the negative sign for y of Rb2 gives −0.1561 equivalent to 0.8439 plus $\frac{1}{2}$ gives 0.3439, which differs by 0.0087 from the y of Rb1.

The ordering of the ions in Table I was done early in the structure refinement. After completing the refinement by least squares, the projection of the structure down the b-axis (Fig. 1) indicated that there could be a better choice of pairs. The projection shows "pseudocenters," halfway between, e.g., Cl7 and Cl8, Cl5 and Cl6, Cl2 and Cl14, Cl1 and Cl13.

Choosing the last pair gives as the x and z coordinates of the pseudocenter: 0.6870 and 0.6333, respectively. Shifting the origin by (−0.6870, 0, −0.6333) puts it at a pseudo-twofold screw axis. Also, in the International Tables for X-Ray Crystallography, the glide plane in $P2_1/a$ is shifted $b/4$ with respect to *Pa*, and the screw axes in $P2_1/a$ are at $\pm a/4$ with respect to *Pa*. Therefore the origin was shifted an additional $(-\frac{1}{4}, -\frac{1}{4}, 0)$; the total shift was then $(-0.9370, -\frac{1}{4}, -0.6333)$.

The pseudocenters produced the following pairs, for Rb: 1–5, 2–6, 3–8, 4–7; for Cu: 1–4, 2–3, 5–8, 6–7, 9–10; for Cl: 1–13, 2–14, 3–11, 4–12, 5–6, 7–8, 9–15, 10–16, 17–18. Least-squares refinement was carried out with the first set relative to the new origin. Remarkably, the final R value was 0.045, only 0.011 greater than for the refinement in *Pa*. The values of the parameters converged to the *averages* of the appropriate pairs within one standard error; in most cases, very much less than one standard error.

The most significant change from the true structure occurred for Cu6 paired with Cu7. In $P2_1/a$, The Cu6–Cl11 and Cu7–Cl3 distances became equivalent and equal to 2.897(7) Å; effectively Cu7 became more nearly three coordinated. There were also many less important changes in distances.

Nevertheless, it should be emphasized that the structure is definitely acentric. This is shown from the statistical calculations on the $|F_{\mathrm{obs}}|$, as mentioned earlier, completely incorrect peaks given by MULTAN when $P2_1/a$ is used as the space group, and the significantly better R value for the true structure. Most important, a simple test for pyroelectricity gave a positive result.

Appendix: Comments on the Structure of Rb_2CuCl_3

Buerger precession camera photographs of a single-crystal chip of Rb_2CuCl_3, taken with Mo$K\alpha$ radiation, indicate that Rb_2CuCl_3 is orthorhombic (diffraction symmetry *mmm*). Reflections $h0l$ are present only for $h = 2n$ and $0kl$ only for $k + l = 2n$; thus, the probable space groups are $Pnam(D_{2h}^{16})$ or $Pna2_1(C_{2v}^{9})$. The lattice constants determined from the precession photographs are: $a = 12.46(2)$, $b = 12.98(2)$, $c = 4.27(1)$ Å. By comparison, the lattice constants of K_2CuCl_3 are: 12.00(2), 12.55(2), 4.20(2) Å, respectively; K_2CuCl_3 belongs to *Pnam* and its crystal structure has been known for many years (3). The relationship of the lattice constants of the two crystals supports our hypothesis that the crystals of Rb_2CuCl_3 and K_2CuCl_3 are isostructural.

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