Crystal Structures of CsCu$_2$Cl$_2$I and CsCu$_2$ClI$_2$

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Crystals of CsCu$_2$Cl$_2$I belong to the monoclinic space group $P2_1/m$ (C_{2h}^2) with $a = 8.27$, $b = 5.76$, $c = 7.62$ (all ±0.01) Å, $\beta = 108.4 \pm 0.2°$, $Z = 2$. Crystals of CsCu$_2$ClI$_2$ belong to the orthorhombic space group $Cmcm$ (D_{2h}^{17}) with $a = 10.04(\pm0.02)$, $b = 13.05(\pm0.03)$ $c = 5.92(\pm0.01)$ Å, $Z = 4$, and are isostructural with CsCu$_2$I$_3$. In CsCu$_2$ClI$_2$, there are, on the average, $(3.7\ \text{Cl}^- + 4.3\ \text{I}^-)$ ions in the g sites and $(0.3\ \text{Cl}^- + 3.7\ \text{I}^-)$ ions in the c sites. In the structures of CsCu$_2$Cl$_3$, CsCu$_2$Cl$_2$I, CsCu$_2$ClI$_2$, and CsCu$_2$I$_3$, the Cs$^+$ ion lies within a trigonal prism formed by halogenide ions; there are also two more halogenide ions within the coordination sphere giving the Cs$^+$ ion 8-coordination. However, the *detailed* coordination geometry of the Cs$^+$ ion in CsCu$_2$Cl$_2$I is different from that of the Cs$^+$ ion in the other crystals. In all the crystals, the Cu$^+$ ions are tetrahedrally coordinated to the halogenide ions and the tetrahedra form double chains parallel to the short axis. © 1985 Academic Press, Inc.

In a recent paper (*1*) on the solid electrolyte system $(\text{Cs}_{1-y}\text{Rb}_y)\text{Cu}_4\text{Cl}_3(\text{I}_{2-x}\text{Cl}_x)$, it was mentioned that the phases CsCu$_2$Cl$_3$, CsCu$_2$Cl$_2$I, CsCu$_2$ClI$_2$, and CsCu$_2$I$_3$ had not been observed as impurity phases although they exist. The first has been known for many years (*2*) and the structure of the last has been determined recently (*3*). The first and last are isostructural, belong to space group *Cmcm,* and are layered at $c/4$.

The results of our work on the structures of the second and third "compounds" show that CsCu$_2$Cl$_2$I is monoclinic and closely related to the structure of CsCu$_2$Cl$_3$; CsCu$_2$ClI$_2$ is isostructural with CsCu$_2$I$_3$, but is only *partially* disordered. There are solid solution ranges of both structures, but this has not been investigated in detail.

At least part of the reason for investigating the structures of the intermediate compounds was to see the effect, if any, on the Cs$^+$-ion coordination of the changing Cl$^-$/I$^-$ ratio.

1. Experimental

Starting materials were as described in (*1*). The specimens were first prepared by solid-state reaction of a pelletized mixture of reactants in a sealed Pyrex tube containing 0.5 atm of dry N$_2$. After checking with X-ray powder diffraction, a pellet of the specimen was melted in a sealed Pyrex tube containing 0.5 atm of N$_2$ and then annealed at 170°C for 16 hr.

Small pieces of crystal were then put into a sphere grinder (*4*) and attempts made to obtain spheres. Because of the nature of the crystals, this was not entirely successful. The CsCu$_2$Cl$_2$I crystals have a fairly strong cleavage in the (101) plane. Therefore, after many trials, we were forced to work with an almost spherical crystal of 0.20-mm diameter flattened slightly in the [101] direction. In this direction the dimension was 0.16 mm.

Crystals of CsCu$_2$ClI$_2$ were softer than

those of CsCu$_2$Cl$_2$I and they also ground anisotropically tending to be ellipsoids of revolution with major axis parallel to the (short) c axis. The crystal used to obtain the diffraction data had a minor axis of 0.10 mm and a major axis (the rotation axis) of 0.16 mm.

Buerger precession camera photographs taken with Mo$K\alpha$ radiation indicated that crystals of CsCu$_2$Cl$_2$I are monoclinic (diffraction symmetry $2/m$); reflections $0k0$ are present only when $k = 2n$ giving as probable space groups $P2_1/m$ and $P2_1$. Crystals of CsCu$_2$ClI$_2$ have diffraction symmetry mmm; reflections hkl are present only when $h + k = 2n$, reflections $h0l$ are present only when h, $l = 2n$. Thus for CsCu$_2$ClI$_2$ the probable space groups are $Cmcm$, $Cmc2_1$, and $C2cm$. Lattice constants determined from the Buerger precession camera photographs are for CsCu$_2$Cl$_2$I, $a = 8.27$, $b = 5.76$, $c = 7.62$ (all ± 0.01) Å, $\beta = 108.4 \pm 0.2°$; and for CsCu$_2$ClI$_2$, $a = 10.04$ (± 0.02), $b = 13.05$ (± 0.03), $c = 5.92$ (± 0.01) Å.

The data were collected with a Buerger-Supper diffractometer automated by a NOVA 1200 computer. Zr-filtered Mo$K\alpha$ radiation was used in the range $6 \leq 2\theta \leq 55°$ for CsCu$_2$Cl$_2$I; the scan rate was 1.5°/min; the scan width was ($1.7 + 2.6\, Lp$), where L is the Lorentz and p the polarization correction. However, the maximum scan was limited to 9°. For CsCu$_2$ClI$_2$, the range was $6 \leq 2\theta \leq 50°$; the scan rate was 1°/min; the scan width was ($1.7 + Lp$) and the maximum scan was limited to 6°. For both, the background was counted at $\frac{1}{4}$ the scan time, before and after the scan.

The unit cell volumes of CsCu$_2$Cl$_2$I and CsCu$_2$ClI$_2$ are 345 and 776 Å^3 with $Z = 2$ and 4, respectively. The formula weights are 457.91 and 549.25, and the X-ray densities 4.41 and 4.70 g cm^{-3}, respectively. The linear absorption coefficients, μ, are 16.8 and 18.6 mm^{-1}, respectively. Absorption corrections were applied to the CsCu$_2$Cl$_2$I data assuming that the crystal had an aver-

age radius of 0.095 mm. The data from the CsCu$_2$ClI$_2$ crystal were not corrected for absorption.

For CsCu$_2$Cl$_2$I, 867 independent diffraction intensities were measured in the 2θ range; of these 303 were rejected as unobserved, i.e., they had net intensities equivalent to less than 100 counts, 11 others were rejected as "bad" data. For CsCu$_2$ClI$_2$, the total number of independent diffraction intensities measured in the given 2θ range with $l \leq 4$, was 327. Of these 172 were unobserved and 6 rejected as bad data.

2. Determination and Refinement of the Crystal Structures

2.1. CsCu$_2$Cl$_2$I

The lattice constants reported (2) for CsCu$_2$Cl$_3$ (space group $Cmcm$) are $a = 9.49$, $b = 11.88$, $c = 5.61$ Å. At the beginning of the analysis, it was clear that the structure of CsCu$_2$Cl$_2$I is related to that of CsCu$_2$Cl$_3$ by the appropriate transformation of axes: ($\frac{1}{2}$ $\frac{1}{2}$ $0|001|\frac{1}{2}$ $\bar{\frac{1}{2}}$ 0), from orthorhombic to monoclinic. Thus the lattice constants of the primitive cell of CsCu$_2$Cl$_3$ are: 7.60, 5.61, 7.60 Å, $\beta = 103°$. As given under Section 1, the lattice constants of CsCu$_2$Cl$_2$I are 8.27, 5.76, 7.62 Å, $\beta = 108.4°$. The increased volume and distortion are caused by the substitution of the I$^-$ for the Cl$^-$.

The transformation of coordinates from the C-centered to the primitive cell is given by ($110|001|1\bar{1}0$). Thus the starting parameters for CsCu$_2$Cl$_2$I were taken to be those

Ion	Position	x	y	z
Cs$^+$	$2e$	-0.317	$\frac{1}{4}$	0.317
Cu$^+$	$4f$	-0.164	0.000	-0.164
Cl$^-$1	$2e$	-0.384	$\frac{1}{4}$	-0.180
Cl$^-$2	$2e$	0.180	$\frac{1}{4}$	0.384
I$^-$	$2e$	0.120	$\frac{1}{4}$	-0.120

TABLE II

FINAL PARAMETER VALUES AND ESTIMATED STANDARD ERRORS FOR $CsCu_2Cl_2I$

Ion:	Cs^+	Cu^+	Cl^-1	Cl^-2	I^-
Position:	$2e$	$4f$	$2e$	$2e$	$2e$
x	−0.3451(4)	−0.1660(4)	−0.394(1)	0.246(1)	0.0908(3)
y	$\frac{1}{4}$	0.0020(9)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
z	0.3382(4)	−0.1296(5)	−0.143(1)	0.386(1)	−0.1791(3)
β_{11}	0.0174(4)	0.0184(6)	0.012(1)	0.022(2)	0.0134(4)
β_{22}	0.047(1)	0.056(2)	0.035(4)	0.037(4)	0.046(1)
β_{33}	0.0225(5)	0.0241(7)	0.021(2)	0.017(2)	0.0167(4)
β_{12}	0	0.000(2)	0	0	0
β_{13}	0.0052(8)	0.004(1)	0.001(3)	−0.001(3)	0.0043(6)
β_{23}	0	−0.001(2)	0	0	0
B_{eqv}	5.26(7)	5.9(1)	4.3(2)	5.0(3)	4.44(6)

Note. The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The form of the equivalent isotropic thermal parameter is $B_{eqv} = 4/3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \alpha + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha]$.

transformed from the $CsCu_2Cl_3$ structure (2), as shown in Table I. The starting most probable space group was chosen to be $P2_1/m$. Because it was expected that the halogenide ions would be ordered, the I^- ions were initially assigned to positions analogous to those of Cl(II) in the $CsCu_2Cl_3$ structure (2) (see Discussion).

In the calculations (which were done with the SDP package on the PDP11, supplied by Molecular Structure Corp., modified for ions), the atomic scattering factors were taken from Volume 4 of the "International Tables for Crystallography." Corrections for both the real and imaginary parts of the anomalous dispersion were included. The final discrepancy factor $(\Sigma|F_o| - |F_c|)/\Sigma|F_o|$ is 0.073 for the 553 reflections included in the calculations.

It should be mentioned that in the course of the calculations, tests were made to determine whether there was mixing of the halogenide ions on the three sites; it was concluded that the structure is completely ordered.

The final parameters and their estimated standard errors are given in Table II.

2.2. $CsCu_2ClI_2$

In this case, the crystals appear to be at least isomorphous with $CsCu_2I_3$ (3), which is isostructural with $CsCu_2Cl_3$ (2). There are four possibilities for the distribution of the halogenide ions: (1) they are completely disordered over the two sets of sites labeled I_1 and I_2 in Ref. (3); (2) they are completely ordered, i.e., the I^- ions are in $8g$ and the Cl^- ions are in $4c$ in space group $Cmcm$; (3) they are partially disordered with all the chlorides and half the iodides in $8g$, and the remaining iodides in $4c$; (4) they are partially disordered with iodides predominating in both sites.

Because of the manner in which the halogenide ions order in $CsCu_2Cl_2I$, it did not seem that either of the first two possibilities was probable. The most probable appeared to be the third, again mainly because of the results obtained for the $CsCu_2Cl_2I$ structure. All the possibilities were tested, however.

Unfortunately, the crystal did not yield many independent observed data. The lowest R value, 0.071, for the 149 structure am-

TABLE III

FINAL PARAMETER VALUES AND ESTIMATED
STANDARD ERRORS FOR $CsCu_2ClI_2$

Atom:	Cs^+	Cu^+	$(Cl_{0.435}I_{0.565})$	$(Cl_{0.07}I_{0.93})$
Position:	$4c$	$8e$	$8g$	$4c$
x	0	0.8472(8)	0.7146(6)	0
y	0.6702(5)	0	0.8844(4)	0.1247(3)
z	$\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{4}$
β_{11}	0.042(1)	0.0210(9)	0.0209(8)	0.0215(7)
β_{22}	0.0134(5)	0.0117(4)	0.0131(4)	0.0070(3)
β_{33}	0.030(2)	0.048(3)	0.030(2)	0.024(2)
β_{12}	0	0	−0.011(1)	0
β_{13}	0	0	0	0
β_{23}	0	0.005(3)	0	0
B_{eqv}	10.2(2)	7.7(2)	7.2(2)	5.6(1)

plitudes was obtained for the distribution: (3.7 Cl⁻ + 4.3 I⁻) in $8g$ and (0.3 Cl⁻ + 3.7 I⁻) in $4c$. The third possibility gave an R value of 0.077.

The starting parameters were those reported for $CsCu_2I_3$ (3). The final parameters and their estimated standard errors are given in Table III.

2.3. Interionic Distances

The interionic distances and their standard errors are given in Table IV.

3. Discussion

As mentioned earlier, our purpose in these studies was to determine the effect of the mixed halogenide content on the Cs^+ coordination. In the end members $CsCu_2Cl_3$ (2) and $CsCu_2I_3$ (3), the Cs^+ ion lies in a trigonal prism with four short and two long Cs^+-X^- distances (where X^- is the halogenide). The longer distances are those to the halogenides in $4c$ positions, i.e., the $X2$. There are also four more distances between Cs^+ and $X1$ ions: there is one through each of two faces, and two through the third face. In $CsCu_2I_3$, the four different distances are (4) 3.861, (2) 4.081, (2) 4.038, (2) 4.466 Å. The last is probably too long to be included in the coordination; thus it may be concluded that in $CsCu_2I_3$ (and in $CsCu_2$-

Cl_3), Cs^+ has 8-coordination. The weighted average of the eight distances is 3.960 Å. In CsI (5), the 8-coordination distance is 3.955 Å.

This coordination persists in $CsCu_2ClI_2$ (see Fig. 1) with the Cl⁻ ions having an almost exclusive preference for the $8g$ sites, and the $4c$ sites preferring almost exclusive occupation by the I⁻ ions; these are the sites that give the longer distances within the trigonal prism. The three distances analogous to those in $CsCu_2I_3$ are (4) 3.73, (2) 3.99, (2) 4.01. The weighted average of these is 3.86 Å. In CsCl (6), the Cs^+-Cl^- 8-coordination distance is 3.571 Å. The weighted average for (2CsI + CsCl) is 3.83

TABLE IV

INTERIONIC DISTANCES (Å) AND STANDARD ERRORS

	$CsCu_2Cl_2I$	
Cs–Cl1	(2)3.626(6),	3.56(1)
–Cl2	(2)3.509(6),	3.51(1)
–I	(2)3.976(3),	4.262(7)

In each triangle in the prism about Cs^+

I–Cl1	4.18(1)
–Cl2	3.92(1)
Cl1–Cl2	3.87(1)
Cu–Cl1	2.342(8)
–Cl2	2.356(8)
–I	2.667(5), 2.683(5)
I–Cl1	4.091(7), 4.10(1)
–Cl2	3.972(7), 4.09(1)
–I	4.539(5)
Cl1–Cl2	3.83(1)

$CsCu_2(Cl_{0.465}I_{0.535})_2(Cl_{0.07}I_{0.93})$

Cs–X	(4)3.731(4), (2)4.003(8), (2)4.307(9)
–I	(2)3.991(6)

In each triangle in the prism about Cs^+

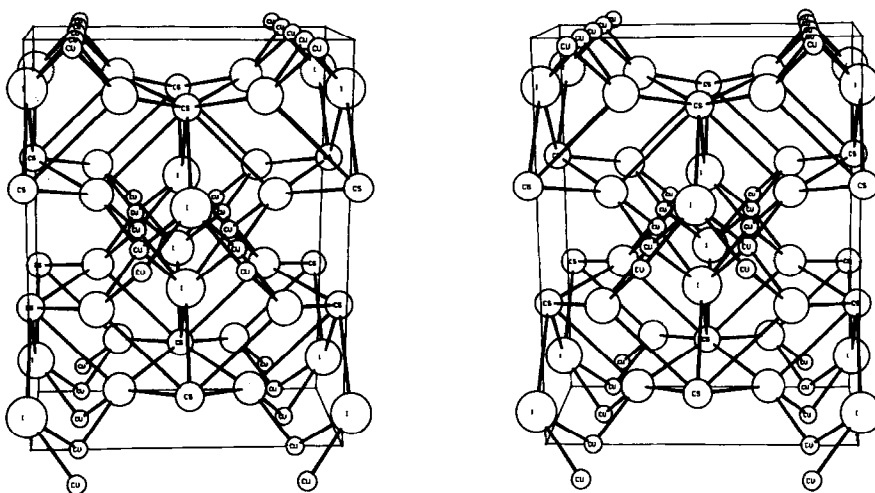|	
X–X	4.31(1)
–I	(2)4.015(7)
Cu–X	(2)2.498(6)
–I	(2)2.682(6)
X–X	4.228(9)
–I	(2)4.248(7), (2)4.123(5)
I–I	4.401(7)

Note. Here X ≡ $(Cl_{0.465}I_{0.535})$, I ≡ $(Cl_{0.07}I_{0.93})$.

FIG. 1. Stereoscopic drawing of the structure of $CsCu_2ClI_2$ looking approximately along c, i.e., the unit cell is rotated 12° counterclockwise about the a axis. The ions labeled I are $(Cl_{0.07}I_{0.93})$; the unlabeled ions are $(Cl_{0.435}I_{0.565})$.

Å. **The agreement is not as good as for $CsCu_2I_3$, but it is close, considering the disorder in $CsCu_2ClI_2$.**

In $CsCu_2Cl_2I$, the Cs^+ ions still have 8-coordination to halogenide ions, but it is different in detail from that in the other three structures. In this case, a trigonal prism formed by four Cl^- ions and two I^- ions still encloses the Cs^+ ion. The coordination is completed by bonds to two Cl^- ions, through the faces of the trigonal prism. Note (see Figs. 2 and 3) that these two Cl^- ions belong to *different* double chains of halogenide tetrahedra. However, in the other three compounds, the two halogenide ions bonded to the Cs^+ ion through the prism faces belong to the *same* double chain. In $CsCu_2Cl_3$, the Cs^+ ion is coordinated to two Cl^- ions at distances of 3.70 Å through the prism faces. There are two other Cl^- ions at distances of 3.97 Å from the Cs^+ ion, which excludes them from the coordination (2). In $CsCu_2Cl_2I$, one of the distances analogous to the 3.70-Å distance in $CsCu_2Cl_3$ decreases to 3.51 Å. The other increases to 4.10 Å, which excludes it from coordination. One of the distances analogous to the

3.97-Å distance in $CsCu_2Cl_3$ decreases to 3.56 Å, which includes it in the coordination, and the other increases to 4.79 Å. Thus, two Cl^- ions remain coordinated to the Cs^+ ion through the prism faces. The weighted average distance between the Cs^+ ion and the halogenide ions is 3.66 Å, to be compared with 3.698 Å derived from the distances in CsCl and CsI. The weighted average of the Cs^+–Cl^- distances is 3.56 Å,
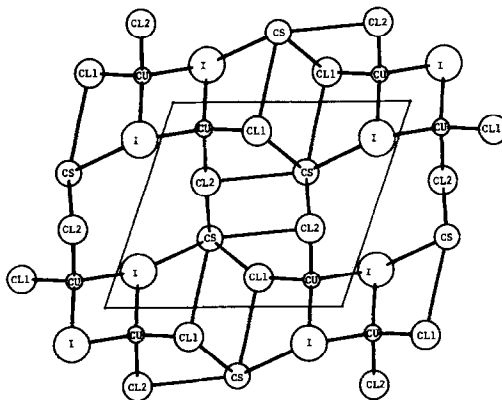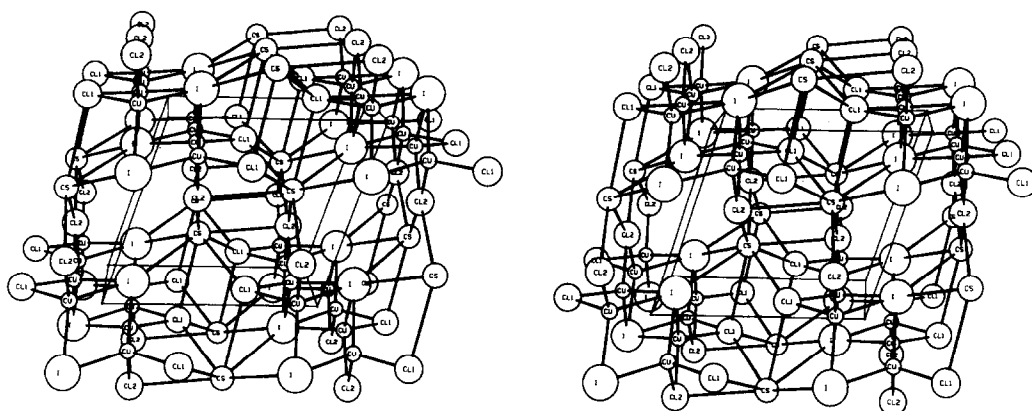

FIG. 2. Projection of the structure of $CsCu_2Cl_2I$ down the b axis.

FIG. 3. Stereoscopic drawing of the structure of $CsCu_2Cl_2I$ looking approximately along b, i.e., the unit cell is rotated 12° counterclockwise about the a axis.

not significantly different from the $Cs^+–Cl^-$ distance in CsCl.

It should be noted that at least in the cubic solid electrolyte phase of $CsCu_4Cl_3I_2$ (*1, 7*), the coordination of the Cs^+ ions is six.

In $CsCu_2Cl_3$, the Cl^- ions in the $4c$ positions are situated such that they effectively join the two chains of halogenide tetrahedra. It can be seen immediately in Figs. 2 and 3, why the I^- ions prefer the analogous sites in $CsCu_2Cl_2I$. This preference is actually least disruptive to the basic structure. It leaves the double chains of tetrahedra intact and indeed leaves all the coordinations of both anions and cations *essentially* unchanged, notwithstanding the change in the *detailed* geometry of the Cs^+-ion coordination relative to that in the other structures. The distortion of the structure because of the increased $I^-–Cl^-$ and $Cs^+–I^-$ distances creates voids along the b axis (see Figs. 2 and 3), resulting in the cleavage that the other crystals do not have. It can be seen that the ($\bar{1}01$) cleavage can pass through the voids without cutting $Cu^+–X^-$ bonds.

As in $CsCu_2I_3$ (*3*) and $CsCu_2Cl_3$ (*2*), the Cu^+ ions are tetrahedrally coordinated to halogenide ions and the tetrahedra form double chains. In $CsCu_2ClI_2$ (Fig. 1) these

chains are along the c axis, the tetrahedra sharing edges perpendicular to the c axis. In $CsCu_2Cl_2I$ (Figs. 2 and 3), the chains are along the b axis and the shared edges are perpendicular to the b axis.

Unfortunately almost all the thermal vibrations **are calculated** to **be much larger** in these crystals than found in $CsCu_2I_3$ (*3*). This is probably only partially a result of inaccurate or no absorption corrections. In $CsCu_2ClI_2$ the high values may be caused in part by the disorder.

In determining the distribution of the halogenide ions in $CsCu_2ClI_2$, the starting distribution was $(4\ Cl^- + 4\ I^-)$ in g and $4\ I^-$ in c. Then the multiplicities were allowed to vary, following which the atomic scattering factors were adjusted to account for the changes in the multiplicities. Thus standard errors on the distributions are not known. As stated earlier it seemed that the above starting distribution was the most probable **one. This is implied by the structure of** $CsCu_2Cl_2I$, **in which the Cl^- ions fill the sites analogous to the $8g$ sites in *Cmcm*, and I^- ions fill the sites analogous to the $4c$ sites in *Cmcm*. Thus, despite the somewhat higher R value for the third possibility, it cannot be definitely ruled out.**

Acknowledgments

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