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# The Crystal Structure of $K_2AgI_3$ and Isomorphous Substances*

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$K_2AgI_3$ is orthorhombic with cell dimensions: $a = 19{\cdot}52$, $b = 9{\cdot}98$, $c = 4{\cdot}74$ Å. The axial ratios are in agreement with the values derived by Penfield from crystallographic measurements, if his $b$ axis is halved. There are four molecules in the cell and the space group is *Pbnm*. Weissenberg diagrams have been taken along the $c$ axis with Mo $K\alpha$ radiation and the positions of the atoms have been fixed by 'trial and error' and by a Fourier projection along the $c$ axis.

The structure is closely related to that of $K_2CuCl_3$. All atoms lie in two symmetry planes perpendicular to the $c$ axis. There are chains of composition $AgI_3$ in the direction of the $c$ axis, with structure analogous to the chains in $K_2CuCl_3$, although their packing is quite different. The surroundings of the potassium ions are very similar. In both structures they are situated between the chains and are surrounded by six halogen ions at the corners of a trigonal prism and one more halogen ion on a lateral face.

$Rb_2AgI_3$ and $(NH_4)_2AgI_3$ are approximately isomorphous with $K_2AgI_3$ and are shown to have the same structure.

## Introduction

In their description of compounds of composition $A_2^IB^I(\text{Hal.})_3$ Wells, Wheeler & Penfield (1892) assumed that $Rb_2AgI_3$ and $K_2AgI_3$ were isomorphous with $Cs_2AgCl_3$. In the first paper of this series (Brink & MacGillavry, 1949) it was found that $Cs_2AgCl_3$, $Cs_2AgI_3$ and $K_2CuCl_3$ are isomorphous and that the axes chosen by Penfield are not those of the truly orthorhombic cell. In this paper a structural investigation of another isomorphous series of compounds $K_2AgI_3$, $Rb_2AgI_3$ and $(NH_4)_2AgI_3$ will be described. For these compounds the axes of the orthorhombic unit cell found by X-ray methods have the same orientation as those chosen by Penfield. Thus there is no longer an apparent isomorphism between the two series.

$K_2AgI_3$, $Rb_2AgI_3$ and $(NH_4)_2AgI_3$ were prepared by saturating a warm concentrated solution of the alkali iodide with silver iodide. They are colourless needles which do not decompose in air.

## The unit cell, space group and atomic positions

$K_2AgI_3$, $Rb_2AgI_3$ and $(NH_4)_2AgI_3$ are orthorhombic. The cell dimensions (Table 1) were determined from oscillation diagrams about the needle axis [001] with Cu $K\alpha$ radiation. The axial ratio found for $K_2AgI_3$, $a:b:c = 1{\cdot}956:1:0{\cdot}475$, is in agreement with Penfield's axial ratio if his $b$ period is halved, giving $1{\cdot}954:1:0{\cdot}468$.

Table 1. *Cell dimensions*

| | $a$ (Å) | $b$ (Å) | $c$ (Å) |
|---|---|---|---|
| $K_2AgI_3$ | $19{\cdot}52 \pm 0{\cdot}02$ | $9{\cdot}98 \pm 0{\cdot}02$ | $4{\cdot}74 \pm 0{\cdot}04$ |
| $Rb_2AgI_3$ | $20{\cdot}0 \pm 0{\cdot}1$ | $10{\cdot}3 \pm 0{\cdot}1$ | $4{\cdot}9 \pm 0{\cdot}1$ |
| $(NH_4)_2AgI_3$ | $21{\cdot}3 \pm 0{\cdot}1$ | $10{\cdot}9 \pm 0{\cdot}1$ | $4{\cdot}6 \pm 0{\cdot}1$ |

The density of the $K_2AgI_3$-crystals was found to be 3·9 g.cm.$^{-3}$; the calculated density for four $K_2AgI_3$ in the unit cell is 4·08 g.cm.$^{-3}$.

The following reflexions were found on the zero-, first- and second-layer-line Weissenberg diagrams along [001]: $hkl$ all orders, $hk0$ all orders, $h0l$ only for $h+l$ even, $0kl$ only for $k$ even. Thus the space group is *Pbnm* or *Pbn*. The structure was developed on the assumption that the space group was *Pbnm*. This space group has two symmetry planes perpendicular to the $c$ axis at a distance $\frac{1}{2}c$ apart. As in the first series of compounds of composition $A_2^IB^I(\text{Hal.})_3$ (Brink & MacGillavry, 1949), the corresponding reflexions in all even layer lines along [001] are similar and the same is true for the reflexions in the odd layer lines. In this structure, therefore, all atoms are also situated in two planes (001) at a distance $\frac{1}{2}c$ apart. Both the potassium and iodine ions are so large that they must lie in the symmetry planes and not between them. Thus all the atoms lie in the symmetry planes. It was possible to find atomic positions in these planes in agreement with the observed intensities. This justified the choice of *Pbnm* as the space group.

## Structure determination

Comparison of the $c$ periods of $K_2AgI_3$ (4·74 Å) and $K_2CuCl_3$ (4·20 Å) suggests that the chains of tetrahedra of composition $BX_3$ found in $K_2CuCl_3$ also occur in $K_2AgI_3$. Attempts to place these chains in the cell in such a way that the potassium ions could fit into

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* The crystal structure of $K_2AgI_3$ has already been published as part of the doctorate thesis of C. Brink (Leiden, 1950).

the open space between them, led to a trial structure in agreement with the intensities of the lower orders. The co-ordinates of this trial structure are listed in Table 2.

Table 2. *'Trial' parameters for* $K_2AgI_3$

| | $x/a$ | $y/b$ |
|---|---|---|
| Ag | 0·133 | 0·125 |
| I(I) | 0·272 | 0·167 |
| I(II) | 0·061 | 0·375 |
| I(III) | −0·100 | 0·033 |
| K(I) | 0·694 | 0·100 |
| K(II) | 0·597 | −0·125 |

The signs derived from this model were used to calculate a Fourier synthesis of 90 out of the 130 *hk*0 reflexions observed with Mo *Kα* radiation. The structure factors were derived from a zero-layer-line Weissenberg photograph. The intensities were measured by visual comparison with an intensity scale photographed with the same crystal. Correction was made in the usual way with the Lorentz and polarization factors.

In this first Fourier projection some of the atoms had moved rather considerably. In the trial structure both of the potassium ions were surrounded by six iodine ions, but the electron-density map showed that they had to be moved to positions in which they would be surrounded by seven iodine ions. Further Fourier syntheses were made and the result of the third one is given in Fig. 1. The background is still rather uneven, but does not reach a height of more than 15 e.Å$^{-2}$ (the highest peak in the projection reaches 135 e.Å$^{-2}$). As a result of their relatively low scattering power, the potassium ions cannot be located as accurately as the other ions. The final co-ordinates are given in Table 3.

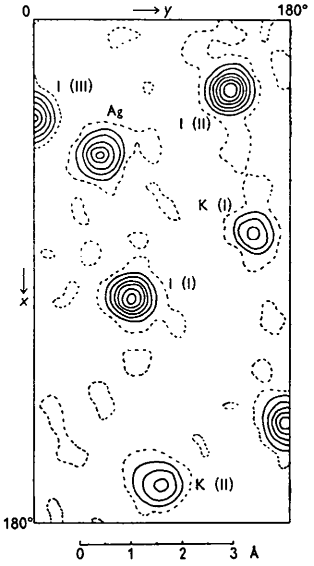

Fig. 1. Electron-density projection of $K_2AgI_3$ along [001]. Contours at intervals of 10 e.Å$^{-2}$ for potassium and 20 e.Å$^{-2}$ for the other atoms. The lowest contour line, at 5 e.Å$^{-2}$, is broken.

Table 3. *Final parameters for* $K_2AgI_3$

| | $x/a$ | $y/b$ |
|---|---|---|
| Ag | 0·135 | 0·129 |
| I(I) | 0·278 | 0·187 |
| I(II) | 0·070 | 0·382 |
| I(III) | −0·099 | 0·008 |
| K(I) | 0·714 | 0·070 |
| K(II) | 0·464 | 0·249 |

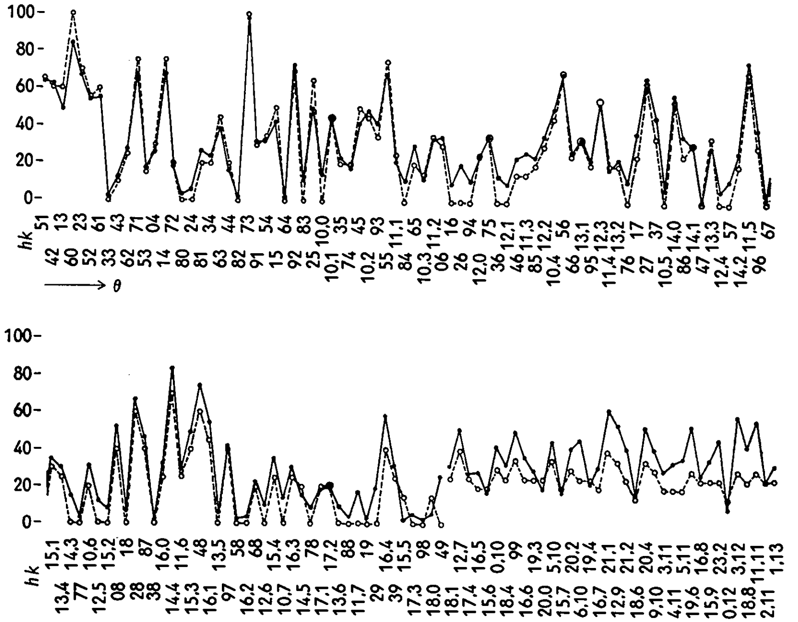

Fig. 2. Structure factors $F(hk0)$ for $K_2AgI_3$. Full line, calculated values; broken line, observed values. Mo *Kα* radiation.

Table 4. *Observed intensities for some lower hkl reflexions of* $K_2AgI_3$ *and corresponding calculated structure factors assuming point atoms.*

| $hk$ | $10^3 \sin^2 \theta_{Cu}$ | $I_{Mo}$ | $F_c$ |
|---|---|---|---|
| 51 | 72 | *ss* | −75 |
| 42 | 75 | — | 0 |
| 13 | 82 | *s* | +82 |
| 23 | 86 | *m* | −43 |
| 52 | 89 | *mw* | −39 |
| 61 | 89 | *w* | −19 |
| 33 | 94 | — | − 1 |
| 70 | 103 | *w* | +33 |
| 43 | 105 | *vw* | −24 |
| 62 | 106 | *w* | +43 |
| 71 | 109 | *ms* | +55 |
| 53 | 119 | *mw* | −42 |
| 04 | 121 | *w* | −47 |
| 14 | 123 | *ms* | −76 |
| 72 | 127 | *w* | +44 |
| 24 | 128 | *w* | +30 |
| 81 | 132 | *s* | +90 |
| 34 | 135 | *s* | −119 |
| 63 | 136 | *ss* | +124 |
| 44 | 146 | *vw* | −35 |
| 82 | 149 | *s* | +87 |
| 90 | 153 | *m* | +65 |
| 73 | 156 | *vw* | −27 |
| 91 | 158 | *m* | −59 |
| 54 | 160 | — | +17 |
| 15 | 177 | *mw* | −55 |
| 64 | 177 | — | +25 |
| 92 | 177 | — | +21 |

Mo $K\alpha$ radiation. *ss* = very strong, *s* = strong, *ms* = medium-strong, *m* = medium, *mw* = medium-weak, *w* = weak, *vw* = very weak.

The structure factors $F(hk0)$ were calculated with the co-ordinates derived from the second electron-density map and the scattering powers tabulated in the *Internationale Tabellen.* No temperature factor was applied. These structure factors and the corresponding experimental ones are shown in Fig. 2. Table 4 compares the observed intensities for some lower reflexions $hkl$ with the structure factors calculated for point atoms. Table 5 gives the calculated distances in $K_2AgI_3$ and, for comparison, also the Ag–I and the K–I distances in AgI and KI.

## Isomorphous substances

The other substances investigated were $Rb_2AgI_3$ and $(NH_4)_2AgI_3$. Table 6 gives for some lower-order reflexions the intensities observed for these compounds and the structure factors calculated assuming that the co-ordinates are the same as found for $K_2AgI_3$. There are some discrepancies between the observed intensities and the calculated structure factors, but this may be a result of small differences in the parameters. The agreement seems good enough to conclude that both $Rb_2AgI_3$ and $(NH_4)_2AgI_3$ are isostructural with $K_2AgI_3$.

## Discussion of the structure

The structure of $K_2AgI_3$ is very like that of $K_2CuCl_3$, as can be seen by comparing the projections of the

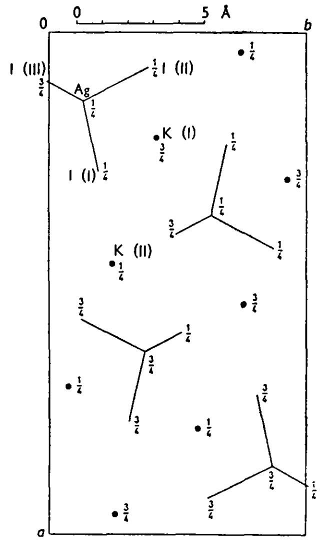

Fig. 3. Projection of the unit cell of $K_2AgI_3$ along [001]. There are four chains of tetrahedra in the direction of the $c$ axis. Ag is at the centres of the tetrahedra, I at the corners. The surroundings of K(I) at $z = \frac{3}{4}$ are: 1 I at $z = \frac{3}{4}$, 3 I at $z = \frac{1}{4}$ and 3 I at $z = \frac{5}{4}$. The surroundings of K(II) at $z = \frac{1}{4}$ are: 3 I at $z = \frac{1}{4}$, 2 I at $z = \frac{3}{4}$ and 2 I at $z = -\frac{1}{4}$.

Table 5. *Calculated distances in* $K_2AgI_3$

Maximum error in the distances about 0·05 Å, in the distances to K(I) and K(II) about 0·1 Å.

| | | | |
|---|---|---|---|
| Ag–I(I) | In the same symmetry plane | (1×) | 2·85 Å |
| Ag–I(II) | In the same symmetry plane | (1×) | 2·82 |
| Ag–I(III) | In different symmetry planes | (2×) | 2·83 |
| K(I)–I(III′) | In the same symmetry plane | (1×) | 3·70 |
| K(I)–I(II) | In different symmetry planes | (2×) | 3·71 |
| K(I)–I(I) | In different symmetry planes | (2×) | 3·62 |
| K(I)–I(I′) | In different symmetry planes | (2×) | 3·49 |
| K(II)–I(I) | In the same symmetry plane | (1×) | 3·68 |
| K(II)–I(III″) | In the same symmetry plane | (1×) | 3·69 |
| K(II)–I(II″) | In the same symmetry plane | (1×) | 3·72 |
| K(II)–I(III′) | In different symmetry planes | (2×) | 3·61 |
| K(II)–I(II′) | In different symmetry planes | (2×) | 3·41 |
| Ag–I | In AgI with zincblende structure | | 2·80 |
| K–I | In KI | | 3·52 |

Table 6. *Observed intensities and calculated structure factors* $F(hk0)$ *for the lower orders of* $Rb_2AgI_3$ *and* $(NH_4)_2AgI_3$ *computed with the parameters found for* $K_2AgI_3$.

| | $Rb_2AgI_3$ | | $(NH_4)_2AgI_3$ | |
|---|---|---|---|---|
| *hk* | $I_{Cu}$ | $F_c$ | $I_{Cu}$ | $F_c$ |
| 21 | *ss* | +30 | *ms* | +37 |
| 31 | *m* | −18 | *w* | −33 |
| 02 | — | — | — | +11 |
| 40 | *w* | −19 | *ms* | −44 |
| 12 | *ms* | +16 | *w* | +35 |
| 22 | *vw* | + 6 | *m* | +40 |
| 41 | — | + 9 | *w* | +40 |
| 32 | *ms* | −35 | *ms* | −50 |
| 51 | *s* | −79 | *w* | −57 |
| 42 | *s* | −65 | *s* | −61 |
| 13 | *s* | +49 | *m* | +51 |
| 60 | *ss* | −85 | *s* | −85 |
| 23 | *ss* | +83 | *ms* | +59 |
| 52 | *ms* | −56 | *w* | −52 |
| 61 | *ms* | −64 | *m* | −51 |
| 33 | — | + 5 | — | + 1 |
| 43 | *w* | +12 | *vw* | +12 |
| 62 | *vw* | −26 | *vw* | −26 |
| 71 | *s* | +82 | *m* | +61 |
| 53 | *w* | −19 | *m* | −16 |
| 04 | *m* | −16 | *m* | −31 |
| 14 | *ss* | −83 | *ms* | −60 |
| 72 | *w* | −21 | — | −18 |
| 80 | — | −18 | *m* | + 5 |
| 24 | *m* | +23 | — | − 2 |
| 81 | — | + 7 | *vw* | +36 |
| 34 | *ms* | +33 | *w* | +19 |
| 63 | *ms* | +70 | — | +24 |
| 44 | *vw* | +21 | *vw* | +13 |
| 82 | — | + 4 | — | − 1 |
| 73 | *s* | −96 | *ss* | −99 |
| 91 | *w* | −22 | — | +36 |
| 54 | *m* | −38 | *w* | −29 |
| 15 | *ms* | +44 | *m* | +43 |
| 64 | — | − 2 | — | + 2 |
| 92 | *ms* | +83 | *m* | +68 |
| 83 | *vw* | −11 | *w* | −11 |
| 25 | *ms* | −52 | *w* | −49 |
| 10,0 | — | +14 | *w* | +14 |
| 10,1 | *s* | −48 | *w* | −42 |
| 35 | *vw* | +14 | — | +28 |
| 74 | *vw* | +12 | *w* | +21 |
| 45 | *ms* | −63 | *vw* | −30 |
| 10,2 | *s* | +69 | *w* | +38 |
| 93 | *m* | +40 | *s* | +43 |
| 55 | *ms* | −60 | *ss* | −73 |
| 11,1 | *w* | +25 | — | +19 |
| 84 | — | + 6 | *vw* | +14 |
| 65 | *vw* | +26 | *w* | +32 |

unit cells given in Figs. 3 and 4. In both structures chains of tetrahedra run in the direction of the *c* axis, though in $K_2AgI_3$ the tetrahedra are more regular than in $K_2CuCl_3$. The surroundings of the potassium ions are also very similar: the ions named K(I) in the two structures have nearly identical immediate surroundings, and the same applies to the ions named K(II). In $K_2AgI_3$ the seven iodine ions round K(I) belong to two chains of tetrahedra: four to one chain and three to the other; in $K_2CuCl_3$, however, this 4:3 arrangement is replaced by 4:2:1. Round K(II) the arrangements are 3:2:1:1 in $K_2AgI_3$ and 3:3:1 in $K_2CuCl_3$. In both structures the surroundings of the negative ions by the positive ions is such that the electrostatic valence rule of Pauling (1939) is satisfied.

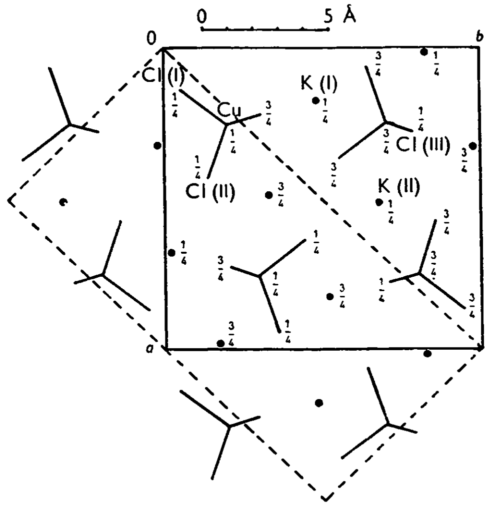

Fig. 4. Projection of the unit cell of $K_2CuCl_3$ along [001]. Broken lines: half of Penfield's pseudo-orthorhombic cell.

Fig. 4 shows the relationship between the true unit cell and Penfield's pseudo orthorhombic cell of $K_2CuCl_3$. If half of Penfield's cell is compared with the unit cell of $K_2AgI_3$ it is seen that the dimensions of these cells are very similar, but the packing of the chains is quite different.

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