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# The Crystal Structures of $(NH_4)_2CuCl_3$ and $(NH_4)_2CuBr_3$*

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$(NH_4)_2CuCl_3$ is orthorhombic with $a$ = 14·71, $b$ = 22·07, $c$ = 4·08 Å. There are eight molecules in the cell and the space group is *Cmmm*. As in $K_2CuCl_3$ and in $K_2AgI_3$, all the atoms lie in two symmetry planes perpendicular to the $c$ axis. The positions of the atoms have been fixed by Patterson and Fourier projections along the $c$ axis. Both optical syntheses with Huggins masks and calculation with Beevers–Lipson strips were used. The structure is related to those of $K_2CuCl_3$ and $K_2AgI_3$ and contains the same type of chains of composition $CuCl_3$ formed by $CuCl_4$ tetrahedra sharing corners. Between these chains parallel to the $c$ axis, three of the $NH_4$ ions are surrounded by eight Cl at the corners of a distorted cube and one $NH_4$ ion is surrounded by six Cl at the corners of a distorted trigonal prism and two more Cl on a lateral face at a somewhat greater distance.

$(NH_4)_2CuBr_3$ is isomorphous with $K_2CuCl_3$, so each $NH_4$ ion is surrounded by seven Br, six at the corners of a distorted trigonal prism and one on a lateral face.

A survey is given of those crystal structures of composition $A_2^IB^I(\text{Hal.})_3$ thus far investigated.

## Introduction

The structure determination of $(NH_4)_2CuCl_3$ and $(NH_4)_2CuBr_3$ continues the investigation of compounds of the general composition $A_2^IB^I(\text{Hal.})_3$ carried out in this laboratory (Brink & MacGillavry, 1949; Brink & Stenfert Kroese, 1952).

$(NH_4)_2CuCl_3$ and $(NH_4)_2CuBr_3$ were prepared and described by Wells & Hurlburt (1895). From their description Groth (1906–19) assumed that these compounds were isomorphous with the other $A_2B(\text{Hal.})_3$ compounds described by Wells, Wheeler & Penfield (1892).

A preparation based on the method of Wells & Hurlburt gave the crystals used in this investigation. A solution of the cuprous halide was obtained from a solution of the cupric halide in the corresponding concentrated hydrogen acid by reduction with copper turnings on a steambath. After the air had been driven out by carbon dioxide, the ammonium halide was added and the heating was continued for some time. On cooling the solution, colourless needles of the complex products were formed. When exposed to the air the crystals turned rapidly brown and afterwards green, especially when they were not completely dry. The crystals used for the X-ray photography were sealed in a Lindemann capillary.

## The crystal structure of $(NH_4)_2CuCl_3$

### *The unit cell, space group and atomic positions*

$(NH_4)_2CuCl_3$ is orthorhombic. The $a$ and $b$ periods were determined from oscillation diagrams about the needle axis [001] with Cu $K\alpha$ radiation. The $c$ period was determined less accurately from measurements of the layer-line separations. The results of the measurements are:

$$a=14{\cdot}71\pm0{\cdot}02,\quad b=22{\cdot}07\pm0{\cdot}02,\quad c=4{\cdot}08\pm0{\cdot}04\ \text{Å}\,.$$

The observed density was 2·1 g.cm.$^{-3}$, that calculated for 8 $(NH_4)_2CuCl_3$ in the unit cell is 2·07 g.cm.$^{-3}$.

On the zero-, first- and second-layer-line $c$-axis Weissenberg diagrams the following reflexions were found: $hkl$ only for $h+k$ even, $hk0$ only for $h+k$ even, $h0l$ only for $h$ even, $0kl$ only for $k$ even. The possible space groups are *Cmmm*, *C*222, *Cmm*2, *C*2*mm*, $C222_1$. The decision between $C222_1$ and the other space groups was made by means of the $00l$ reflexions: 001 was present and this excludes the space group $C222_1$.

As in those compounds of composition $A_2B(\text{Hal.})_3$ previously investigated, the intensities of corresponding reflexions in all observed even layer lines along the $c$ axis are similar, and the same applies to the reflexions in the two observed odd layer lines. This means that all atoms are situated in two planes (001) separated by $\frac{1}{2}c$. The space group *Cmmm* has two symmetry planes (001) at $z = 0$ and $z = \frac{1}{2}$. Both $NH_4$ and Cl are too large to be located between these planes, 2·04 Å apart. Therefore, if the space group is *Cmmm*, the centres of all atoms have to be placed in the symmetry planes. It is possible to find an arrangement of the atoms in these planes in agreement with the observed intensities, so the less symmetrical space groups need not be considered.

### *Structure determination*

The intensities of the reflexions on the $c$-axis zero-layer-line Weissenberg photographs taken with Cu $K\alpha$

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* Already published as part of the doctorate thesis of C. Brink (Leiden, 1950).

radiation were estimated by visual comparison with a scale of spots of known exposure and were corrected with Lorentz, polarization and absorption factors. The absorption correction was made by assuming that the crystal was cylindrical, which seemed to be a good approximation.

The distance between the symmetry planes in $(NH_4)_2CuCl_3$ is 2·04 Å, which is nearly equal to the distance between the symmetry planes in $K_2CuCl_3$ (2·10 Å). This suggests that in $(NH_4)_2CuCl_3$ the same chains of tetrahedra as in $K_2CuCl_3$ may run in the direction of the $c$ axis. This is, moreover, in agreement with the optical behaviour of $(NH_4)_2CuCl_3$, as the largest refractive index is in the needle direction. An optical Patterson synthesis of the $F^2(hk0)$ was made by means of the 'Huggins masks' in the hope of finding the position of the copper atoms. The masks available in the laboratory of Professor Bijvoet in Utrecht were for indices up to ten. To make the best use of the data the primitive cell of the structure, a diamond with edges 13·26 Å and angle 66°, was made to correspond with the square cell of the optical synthesis. It was found impossible to fit the assumed chains of tetrahedra into the cell with the copper atom in an eightfold position. The chains could, however, be fitted into the cell and the Patterson projection explained, if the copper atoms occupied the two fourfold positions $4h$ and $4j$ (*Internationale Tabellen*) with approximate parameters $x = \frac{1}{4}$ and $y = \frac{1}{6}$. Packing considerations determined the position of the other atoms. The approximate co-ordinates, found by adjustments of paper circles representing the atoms, are shown in Table 1.

Table 1. *Trial co-ordinates for* $(NH_4)_2CuCl_3$

| | | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|---|
| Cu(I) | (4*h*) | 0·283 | 0 | 0·5 |
| Cu(II) | (4*j*) | 0 | 0·175 | 0·5 |
| Cl(I) | (4*g*) | 0·181 | 0 | 0 |
| Cl(II) | (4*i*) | 0 | 0·114 | 0 |
| Cl(III) | (8*q*) | 0·375 | 0·092 | 0·5 |
| Cl(IV) | (8*q*) | 0·142 | 0·236 | 0·5 |
| $NH_4$(I) | (2*b*) | 0·5 | 0 | 0 |
| $NH_4$(II) | (2*d*) | 0 | 0 | 0·5 |
| $NH_4$(III) | (4*i*) | 0 | 0·319 | 0 |
| $NH_4$(IV) | (8*p*) | 0·222 | 0·144 | 0 |

Assuming this model, the signs of the structure amplitudes $F(hk0)$ were calculated and an optical Fourier synthesis was performed for the same cell as used in the Patterson projection. The result showed clearly the projection of the four $CuCl_3$ chains, but it was not possible to locate the $NH_4$ groups because of their lower scattering power and the low resolving power of the optical method.

An optical Patterson synthesis is less accurate than a calculated one and, moreover, the limited number of masks available caused large termination-of-series errors. It was possible, nevertheless, to deduce a model from the optical Patterson synthesis as the problem was essentially a two-dimensional one and because the structure of the chains occurring in $K_2CuCl_3$ was already known. The peaks in the Patterson picture are more pronounced than might be expected, as many vectors are accidentically equal in this projection.

In order to get more accurate co-ordinates the same Fourier projection was calculated by means of the Beevers–Lipson strips. In this summation the $C$-centred cell was used, because of the simpler form of the series. In the first summation 80 of the available 110 terms were included. A further synthesis of all the structure factors, with the signs based on the positions derived from the first Fourier projection, gave the electron-density map shown in Fig. 1. It was again not possible to derive accurate positions for the $NH_4$ ions from the map, because of their relatively low scattering power. It was found that a small shift of $NH_4$(III) and $NH_4$(IV) from the peak positions would give more equal distances between these ions and the surrounding chlorine ions. Structure-factor calculations showed that the new positions gave slightly better agreement with the observed intensities. The final co-ordinates are listed in Table 2. The observed structure factors $F(hk0)$ and $F(hk1)$, together with those calculated using the atomic scattering factors listed in the *Internationale Tabellen*, are plotted in Fig. 2 and 3.

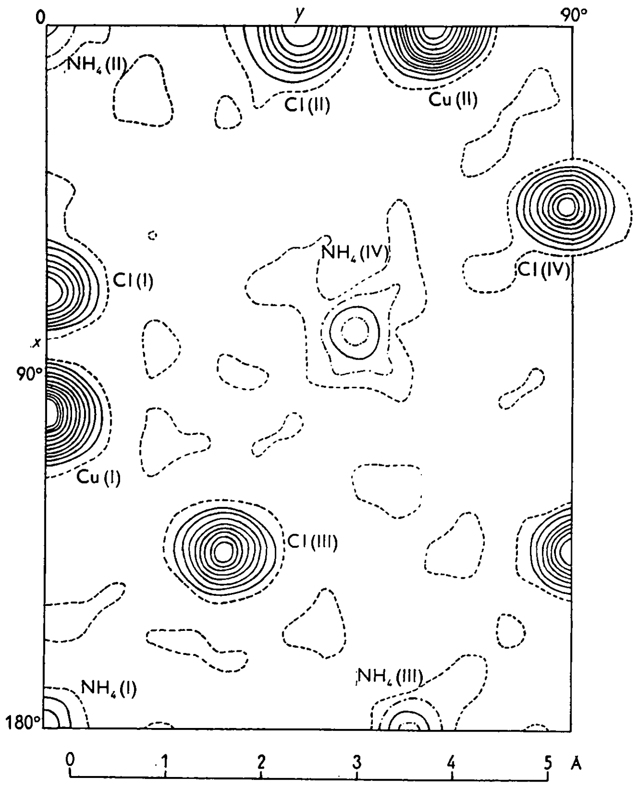

Fig. 1. Electron-density projection of $(NH_4)_2CuCl_3$ along [001]. Contours at intervals of 2 e.Å$^{-2}$ for $NH_4$ and 4 e.Å$^{-2}$ for the other atoms. The lowest contour line, at $2\frac{1}{2}$ e.Å$^{-2}$, is broken.

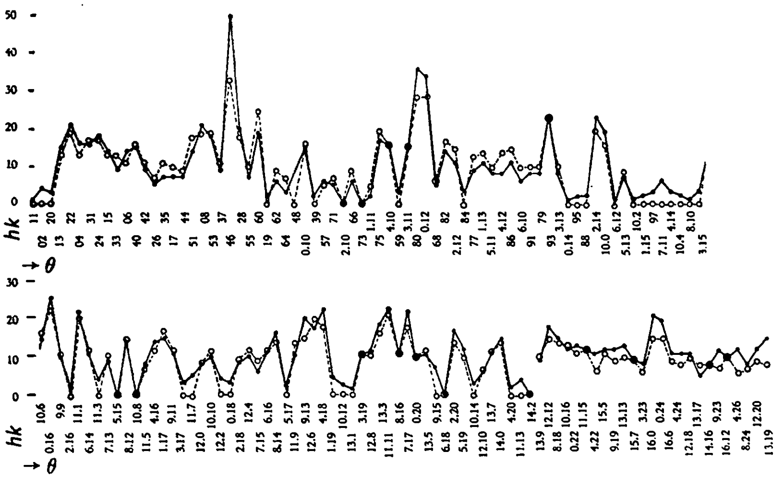

Fig. 2. Structure factors $F(hk0)$ for $(NH_4)_2CuCl_3$. Full line: calculated values; broken line: observed values. Cu $K\alpha$ radiation.

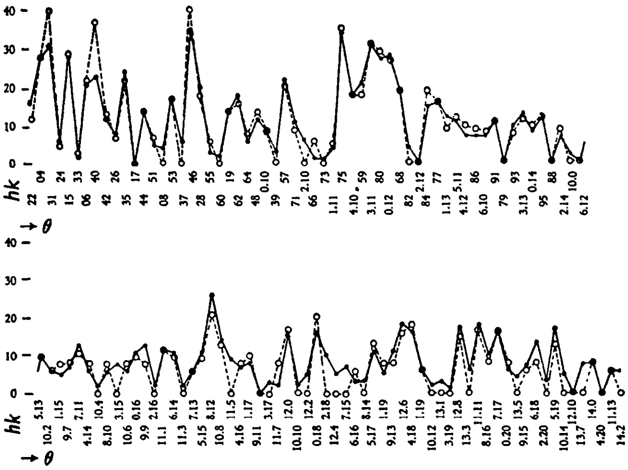

Fig. 3. Structure factors $F(hk1)$ for $(NH_4)_2CuCl_3$. Full line: calculated values; broken line observed values. Cu $K\alpha$ radiation.

In these calculations no temperature factor was applied.

Table 2. *Final co-ordinates for* $(NH_4)_2CuCl_3$

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Cu(I) | 0·278 | 0 | 0·5 |
| Cu(II) | 0 | 0·183 | 0·5 |
| Cl(I) | 0·187 | 0 | 0 |
| Cl(II) | 0 | 0·119 | 0 |
| Cl(III) | 0·373 | 0·085 | 0·5 |
| Cl(IV) | 0·128 | 0·247 | 0·5 |
| $NH_4$(I) | 0·5 | 0 | 0 |
| $NH_4$(II) | 0 | 0 | 0·5 |
| $NH_4$(III) | 0 | 0·330 | 0 |
| $NH_4$(IV) | 0·227 | 0·152 | 0 |

The interatomic distances are listed in Table 3. The Cu–Cl distance in CuCl and the $NH_4$–Cl distance in 'low $NH_4Cl$', having the CsCl-type of structure, are given for comparison.

### *Discussion of the structure*

Fig. 4 gives a projection of the structure along [001]. There are eight chains of composition $CuCl_3$, formed by $CuCl_4$ tetrahedra sharing corners, traversing the unit cell in the direction of the c axis. In the compounds isostructural either with $K_2CuCl_3$ or with $K_2AgI_3$ there are in each unit cell four chains of this type. These $CuCl_3$ chains are more compact than the $SiO_3$ chains in the pyroxenes (Brink & MacGillavry, 1949). In both $K_2CuCl_3$ and $(NH_4)_2CuCl_3$ the distances from a copper atom to the chlorine atoms in its own symmetry plane seem to be slightly shorter than its distances to the chlorine atoms in the neighbouring symmetry planes. In $K_2AgI_3$ the corresponding distances are equal within the limits of the experimental error.

The $NH_4$ ions are placed between the chains so that all are surrounded by eight chlorine ions. $NH_4$(I), $NH_4$(II) and $NH_4$(III), though crystallographically

Table 3. *Calculated distances in* $(NH_4)_2CuCl_3$

Maximum error in the distances about 0·05 Å; in the distances to $NH_4$(III) and $NH_4$(IV) about 0·1 Å.

| | | | |
|---|---|---|---|
| Cu(I)–Cl(III) | In the same symmetry plane | (2×) | 2·34 Å |
| Cu(I)–Cl(I) | In different symmetry planes | (2×) | 2·43 |
| Cu(II)–Cl(IV) | In the same symmetry plane | (2×) | 2·35 |
| Cu(II)–Cl(II) | In different symmetry planes | (2×) | 2·48 |
| $NH_4$(II)–C(I) | In different symmetry planes | (4×) | 3·43 |
| $NH_4$(II)–Cl(II) | In different symmetry planes | (4×) | 3·33 |
| $NH_4$(I)–Cl(III) | In different symmetry planes | (8×) | 3·33 |
| $NH_4$(III)–Cl(III) | In different symmetry planes | (4×) | 3·33 |
| $NH_4$(III)–Cl(IV) | In different symmetry planes | (4×) | 3·33 |
| $NH_4$(IV)–Cl(III) | In different symmetry planes | (2×) | 3·32 |
| $NH_4$(IV)–Cl(IV) | In different symmetry planes | (2×) | 3·27 |
| $NH_4$(IV)–Cl(IV) | In different symmetry planes | (2×) | 3·68 |
| $NH_4$(IV)–Cl(I) | In the same symmetry plane | (1×) | 3·42 |
| $NH_4$(IV)–Cl(II) | In the same symmetry plane | (1×) | 3·43 |
| Cu–Cl | In CuCl | | 2·34 |
| $NH_4$–Cl | In low $NH_4Cl$ | | 3·34 |

non-equivalent, have almost identical environments, being surrounded by eight nearly equidistant chlorines at the corners of slightly deformed cubes. $NH_4$(IV) is surrounded by six chlorines at the corners of a deformed trigonal prism (trigonal axis perpendicular to the *c* axis) and two more chlorines on a lateral face at a somewhat greater distance. The structure may be considered to have both wide and narrow bands with the structure of 'low $NH_4Cl$' running parallel to the *c* axis.

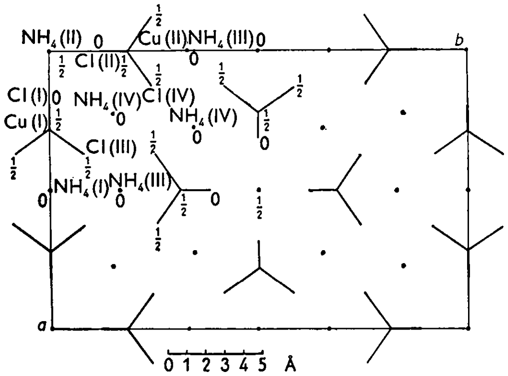

Fig. 4. Projection of the unit cell of $(NH_4)_2CuCl_3$ along [001]. There are eight chains of tetrahedra in the direction of the *c* axis. In the centre of the tetrahedra is Cu, at the corners Cl.

$NH_4$(I) at $z=0$ is surrounded by
4 Cl at $z=\frac{1}{2}$ and 4 Cl at $z=-\frac{1}{2}$.
$NH_4$(II) at $z=\frac{1}{2}$ is surrounded by
4 Cl at $z=0$ and 4 Cl at $z=1$.
$NH_4$(III) at $z=0$ is surrounded by
4 Cl at $z=\frac{1}{2}$ and 4 Cl at $z=-\frac{1}{2}$.
$NH_4$(IV) at $z=0$ is surrounded by
3 Cl at $z=\frac{1}{2}$, 3 Cl at $z=-\frac{1}{2}$ and 2 Cl at $z=0$.

All the chlorine atoms are surrounded by Cu and $NH_4$ in such a way that the structure satisfies the 'electrostatic valence rule' of Pauling (1939).

## The structure of $(NH_4)_2CuBr_3$

$(NH_4)_2CuBr_3$ was found to be isomorphous with $K_2CuCl_3$, as the axial ratios are equal within the limits of experimental error. The cell dimensions are:

| | *a* (Å) | *b* (Å) | *c* (Å) |
|---|---|---|---|
| $(NH_4)_2CuBr_3$ | 13·1±0·1 | 14·0±0·1 | 4·4±0·1 |
| $K_2CuCl_3$ | 12·00±0·02 | 12·55±0·02 | 4·20±0·04 |

(Brink & MacGillavry, 1949.)

The assumption that $(NH_4)_2CuBr_3$ is also isostructural with $K_2CuCl_3$ is confirmed by general agreement between observed intensities and calculated structure factors. These are given for the lower reflexions in Table 4.

## Survey of the structures $A^{I}_{2}B^{I}(\text{Hal.})_3$

Table 5 lists the compounds $A_2B(\text{Hal.})_3$ (where *A* is an alkali ion and *B* copper or silver) thus far investigated, and gives the surroundings of the alkali ions. The *B* ions and the halogen ions form the chains in which the *B* ions are surrounded by four halogen ions. In all the compounds the alkali ions are surrounded by seven halogen ions, except in $(NH_4)_2CuCl_3$ where the $NH_4$ are surrounded by eight chlorine ions. In the corresponding alkali halides the co-ordination numbers of the alkali ions are six or eight. As the radius of the caesium ion is greater than the radius of the $NH_4$ ion it is remarkable that caesium in $Cs_2AgCl_3$ is surrounded by seven chlorine ions, whereas $NH_4$ in $(NH_4)_2CuCl_3$ is surrounded by eight chlorine ions.

More compounds of the composition $A_2B(\text{Hal.})_3$ have been described in literature. A list of the compounds found in melting diagrams of mixtures of *A*Hal. and *B*Hal. is given in *Inorganic Chemistry*

Table 4. *Observed intensities and calculated structure factors, F(hk0), for* $(NH_4)_2CuBr_3$ *computed with the parameters found for* $K_2CuCl_3$.

| *hk*0 | $I_{Cu}$ | $F_c$ | *kk*0 | $I_{Cu}$ | $F_c$ |
|---|---|---|---|---|---|
| 130 | *ms* | +29 | 540 | *s* | −32 |
| 310 | *m* | −15 | 620 | *s* | +38 |
| 230 | *w* | +10 | 360 | — | + 2 |
| 320 | *s* | +37 | 630 | *s* | −36 |
| 040 | *vw* | + 4 | 170 | *m* | −27 |
| 140 | *m* | +16 | 550 | *m* | −22 |
| 400 | *m* | +21 | 270 | *m* | +24 |
| 410 | *s* | −43 | 460 | *m* | +20 |
| 330 | *m* | −15 | 710 | *s* | +42 |
| 240 | *s* | −44 | 640 | *m* | +10 |
| 420 | *ss* | −65 | 720 | — | − 8 |
| 150 | — | 0 | 370 | *vw* | − 4 |
| 340 | *w* | + 7 | 730 | *ms* | −29 |
| 430 | *w* | − 9 | 560 | *s* | −32 |
| 510 | *w* | −14 | 080 | *m* | −31 |
| 250 | *s* | +52 | 650 | *w* | − 1 |
| 520 | *w* | +13 | 180 | *m* | +21 |
| 440 | *vw* | + 5 | 470 | — | + 1 |
| 350 | *m* | +26 | 280 | *m* | +37 |
| 060 | *m* | +20 | 740 | — | 0 |
| 530 | *vw* | − 8 | 800 | *w* | +20 |
| 160 | — | − 1 | 810 | *w* | −16 |
| 600 | *m* | −35 | 380 | — | +10 |
| 260 | *vw* | + 5 | 820 | — | − 1 |
| 610 | — | − 4 | 660 | *m* | −13 |
| 450 | *vw* | +13 | 570 | *s* | +33 |

Table 5. *Survey of the structures* $A_2B(\text{Hal.})_3$

| | Space group | No. of chains surrounding *A*'s | No. of halogen ions surrounding *A* | Arrangement |
|---|---|---|---|---|
| $K_2CuCl_3$ | *Pnam* | 3, 3 | 7 | Trigonal prism with one *A* on a lateral face |
| $Cs_2AgI_3$ | *Pnam* | 3, 3 | 7 | |
| $Cs_2AgCl_3$ | *Pnam* | 3, 3 | 7 | |
| $(NH_4)_2CuBr_3$ | *Pnam* | 3, 3 | 7 | |
| $K_2AgI_3$ | *Pbnm* | 2, 4 | 7 | |
| $Rb_2AgI_3$ | *Pbnm* | 2, 4 | 7 | |
| $(NH_4)_2AgI_3$ | *Pbnm* | 2, 4 | 7 | |
| $(NH_4)_2CuCl_3$ | *Cmmm* | 2, 4, 3, 3 | 8(3×) | Cube |
| | | | 6+2(1×) | Trigonal prism and two *A* on a lateral face at a greater distance |

(A. E. van Arkel, in the press). A structural investigation was carried out only for those compounds of which single crystals could be obtained from aqueous solutions.

The authors wish to thank Prof. Dr C. H. MacGillavry for her great interest in the investigation and Prof. Dr J. M. Bijvoet for allowing them to use the Huggins masks in the van 't Hoff Laboratory in Utrecht.

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