

An X-Ray Refinement of the Crystal Structure of Copper(II) Chloride Dihydrate

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The crystal structure of copper(II) chloride dihydrate was refined using three dimensional diffractometer data (MoK α radiation). The atomic positional parameters are equal to those found by other authors using neutron diffraction, except for a small difference in the oxygen position. Large, strongly anisotropic thermal vibrations are found, especially for the oxygen atoms. Comparing with kinetic dehydration data, the possibility of a correlation between dehydration mechanism and thermal vibration is considered. An expression for the structure factor of oxygen using an aspherical scattering factor is discussed. Finally, some simple correlations between the crystal structure and some optical and physical properties are considered.

The crystal structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ has previously been investigated by Harker.¹ The results of this author were mainly confirmed by a contemporary analysis carried out by Mac Gillavry and Bijvoet.² Further, a neutron diffraction refinement was made by Peterson and Levy.³

The purpose of the present work is primarily to investigate the thermal vibrations, especially of the oxygen atoms. Investigations by Engberg⁴ showed that the crystals, when dehydrated in vacuum at room temperature, in a kinetical sense behave as cubes. However, the normal habit of the crystals is long prisms, *i.e.* the propagation of the surface of reaction is several times faster in the length direction of the crystals than in the direction perpendicular to it.

It is a striking feature of the crystal structure that the water molecules are arranged in columns along the length direction of the crystals. A possible mechanism of the dehydration might be jumps of water molecules between neighbouring positions in the length direction. A pronounced anisotropic vibration of the water molecules might facilitate such jumps.

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By measurements in the far infrared region, Brehat *et al.*⁵ have detected absorption bands at 227.5, 188.5, and 137 cm^{-1} , which they ascribe to the translational vibrations of the water molecules. Further, a band at 298 cm^{-1} was associated to water libration. Itoh *et al.*⁶ have interpreted 4 bands in the region 1300–1800 cm^{-1} as bending vibrations in the water molecules. Rundle *et al.*⁷ used polarized infrared radiation and found that the absorption corresponding to bending of the water molecules (in the region 1450–1700 cm^{-1}) was strongly dependent on the direction of polarization.

A second purpose of the present work is comparison of the results of the X-ray refinement with those of the neutron refinement.³ The latter did not include investigation of the thermal vibrations.

Finally, simple correlations between the crystal structure and some physical and optical properties are discussed.

EXPERIMENTAL

Well developed prismatic crystals of copper chloride dihydrate were obtained by recrystallisation of the Merck *pro analysi* product from a solution acidified by hydrochloric acid (Engberg⁸). After examination of several samples with the polarizing microscope, a typical prismatic crystal was selected. The length was 1.5 mm, and the cross section was a parallelogram with angles $85.35 \pm 0.50^\circ$ (calculated $84.96 \pm 0.20^\circ$) and $94.65 \pm 0.50^\circ$ (calc. $95.04 \pm 0.20^\circ$) and distances 0.20 and 0.15 mm between opposite faces. The angles were measured by reflection goniometry, and the calculated angles with the present choice of axes correspond to the faces [101], the *c*-axis dividing the obtuse angle of the cross section, and the *b*-axis being parallel to the length direction of the crystal. This choice of axes is different from that of Harker.¹

The cell dimensions were determined by the precession method using $\text{MoK}\alpha$ radiation. The reflection intensities of the same crystal were measured with an automatic diffractometer delivered by Stoe et Cie. GmbH, Darmstadt, West Germany. The radiation was $\text{MoK}\alpha$, monochromatized by a LiF single crystal. The constancy of the apparatus and the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ crystal was currently controlled by measurement of a standard reflection. The fluctuations of these measurements were well below the standard deviation calculated from counting statistics, and no systematic trends were found during the period of reflection measurement.

The axis of rotation was *b*, and the symmetrically equivalent reflexions $h0l-h5l$ and $h0l-h5\bar{l}$ were measured in the range $0.12 < \sin\theta/\lambda < 1.0$. Constant time counting and omega-scan with rate 0.1°/min was used. A total of 800 independent pairs of reflections were measured. The intensity of 668 pairs was greater than twice their counting standard deviation.

The temperature was registered continuously near the crystal and was maintained at $28.5 \pm 1.5^\circ$. The dihydrate should be stable at this temperature in the range 35–75 % relative humidity (Dienis⁹). For safety, the crystal was coated with a thin layer of nail varnish.

SPACE GROUP AND UNIT CELL DIMENSIONS

The orthorhombic space group $Pbmn-D_{2h}^7$ reported by Harker¹ was confirmed from Weissenberg and precession photographs. After axial transformation $a' b' c' \rightarrow c a b$, this space group is transformed to $Pmna$, which is the notation of the *International Tables*. For practical reasons and for comparison with the structure of anhydrous CuCl_2 , (Wells¹⁰), the choice of axes of the present work corresponds to $Pmna$. There are 2 formula units in the cell, and the atomic positions are as follows: 2 Cu in *a*, (0,0,0) *etc.*, 4 Cl in *h*, (0,*y*,*z*) *etc.*, 8 H in *i*, (*x*,*y*,*z*) *etc.*, and 4 O in *e*, (*x*,0,0) *etc.*

Table 1. Cell parameters of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

Present work	a	b	c	density (calc.)
Harker notation	b'	c'	a'	
Harker (oscillation)	8.04 Å	3.72 Å	7.38 Å	2.57 g/cm ³
McGillavry <i>et al.</i>	8.06 Å	3.74 Å	7.40 Å	2.54 g/cm ³
Present work (25°C)				
Cross sect. 0.20 × 0.15 mm	8.126 Å (0.008)	3.764 Å (0.005)	7.440 Å (0.007)	2.488 g/cm ³ (0.004)
Present work (28°C)				
Cross sect. 0.025 × 0.05 mm	8.104 Å (0.008)	3.757 Å (0.004)	7.433 Å (0.007)	2.501 g/cm ³ (0.004)

The cell parameters reported in the literature are compared to those of the present work in Table 1.

The calculation of cell parameters and their standard deviations was based on the following considerations:

As proposed by Patterson and Love,¹¹ the expression used for calculation of cell parameter a was the following:

$$a = a_0 \frac{S \Delta w_0}{S_0 \Delta w} \quad (1)$$

Here, a_0 is the cell edge for $\text{Pb}(\text{NO}_3)_2$, a crystal of which was used for calibration. According to *International Tables*, Vol. III, a mean of different literature values is $a_0 = 7.856 \text{ Å} \pm 0.002$ at $26 \pm 3^\circ \text{C}$.

S and S_0 are corresponding distances between fiducial spots on a $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, *viz.* $\text{Pb}(\text{NO}_3)_2$ -film.

Δw and Δw_0 are the weighted mean values of Δ_i/h_i , where Δ_i is the distance measured on the precession film between the two rows of spots corresponding to Miller indices $\pm h_i$. Δw corresponds to $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and Δw_0 to $\text{Pb}(\text{NO}_3)_2$. The same apparatus and wavelength ($\text{MoK}\alpha$) was used for both compounds. The evaluation of Δw and Δw_0 was somewhat different from that proposed by Patterson and Love¹¹ and proceeded as follows:

If n is the number of row pairs corresponding to a single cell parameter, it was assumed that the reading precision was the same for all of the n distances Δ_i belonging to one set of values $i=1, n$. Consequently, the weighting used was $w = 1/\sigma^2(\Delta_i/h_i) = \text{const} \cdot h_i^2$, and the expression for the weighted mean Δw and the squared standard deviation $\sigma^2 \Delta w$ were:

$$\Delta w = \frac{\sum_{i=1}^n \Delta_i h_i}{\sum_{i=1}^n h_i^2}; \quad \sigma^2 \Delta w = \sigma^2 \Delta_i \frac{1}{\sum_{i=1}^n h_i^2}$$

Because of the assumption of equal precision for all values Δ_i , the standard deviation σ_{Δ_i} was simply evaluated as

$$\sigma_{\Delta_i} = \sqrt{\frac{\sum (\Delta_i - h_i \Delta w)^2}{n-1}}$$

The fact that no systematic trends were found in any set of values $\Delta_i - h_i \Delta w$ indicates that systematic errors (for example due to absorption) are small.

Of course, σ_{Δ_i} was different from one set of values to another, depending on the size and elongation of the spots. A vernier calibrated to 0.05 mm (least count 0.025 mm) was used, and standard deviations in the range $0.025 < \sigma_{\Delta_i} < 0.11$ mm were found.

As proposed by Patterson and Love, the square of the total relative standard deviation of a cell parameter was calculated as the sum of squares of the relative standard deviations of a_0 , Δw , Δw_0 , S , and S_0 .

It is difficult to discuss the systematic differences between the parameter values of the literature and those of the present work because of insufficient information about the methods used by the other authors.

The crystal used for diffractometry was rather thick (0.20×0.15 mm), and it was decided to compare the precession cell parameters with those found from a very thin crystal (0.025×0.05 mm) measured with the same apparatus. As will be seen from Table 1, the differences are systematic, the tendency being opposite to what would be expected from absorption error (Buerger¹²) and temperature difference.

According to Engberg,⁸ the density of a fine powder (measured with a pycnometer) is 2.514 ± 0.001 g/cm³ at 25°C. The calculated density of both of the single crystals mentioned in Table 1 is slightly below this value. This indicates a different amount of disorder, and it looks reasonable that the density is greatest for the small crystal. As discussed below, the crystal structure indicates that the cell parameters might vary slightly from one crystal to another.

An attempt to measure the cell parameters from a powder photograph was not successful. Numerous line overlaps rendered the indexing ambiguous, and the high angle lines were broad and diffuse.

CORRECTION OF OBSERVED INTENSITIES

The observed net intensities and their standard deviations from counting statistics were corrected in the following way:

a) The factor $\cos \mu$ was applied to correct for differences between the illuminated volumes corresponding to different values of the setting angle μ .

b) In the LP-correction, the polarization term was calculated under consideration of the primary polarization by the monochromator crystal, this being regarded as ideal perfect (Azaroff¹³).

c) The absorption correction was calculated with a FORTRAN program of the type proposed by Busing and Levy.¹⁴ The theoretical linear absorption coefficient = 58.8 cm⁻¹ was used, and the summation was carried out over 6×6 sampling points. Because of the rectangular cross section of the crystal, the reflexions hkl were generally stronger than the crystallographically equivalent reflexions $h\bar{k}l$ before correction for absorption. The conformity of the two sets of observations after correction appeared to be a very useful check on the absorption correction and a guide to detection of reflexions suffering from counting losses or extinction errors, both of these errors being most

pronounced in the hkl set. In the first place, separate refinement of the two data sets was carried out, the errors in question, if present, being systematic rather than random.

LEAST SQUARES REFINEMENT OF POSITIONAL AND THERMAL PARAMETERS

The initial calculated structure factors were based on the refined atomic parameters from the neutron work by Peterson and Levy.³ The scattering factors were the spherical Hartree-Fock values quoted in the *International Tables*, Vol. II, 1962. This choice was based on the discussion by Cromer.¹⁵ The scattering factors of Cu and Cl were corrected for dispersion according to Cromer.¹⁶

Table 2. Refinement results: positional parameters (X-ray and neutron results compared) and thermal parameters (X-ray results). The parameters not mentioned are equal to zero.

$$\text{Values of } U = \sqrt{\frac{\sum w(F_o - F_c)^2}{n-p}}, R = \frac{\sum |F_o - F_c|}{\sum F_o}, \text{ and } R_w = \sqrt{\frac{\sum w(F_o - F_c)^2}{\sum w F_o^2}}$$

Expression for thermal vibration:

$$f = f_0 \exp[-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + 2hk b_{12} + 2hl b_{13} + 2kl b_{23})].$$

	Neutron work Peterson <i>et al.</i>	Present work 0.50 < sin θ / λ < 1.0	Present work 0.80 < sin θ / λ < 1.0
Cu			
b_{11}		0.00369 (6)	0.00375 (18)
b_{22}		0.0327 (4)	0.0307 (10)
b_{33}		0.00664 (7)	0.00675 (22)
b_{23}		-0.00406 (9)	-0.00391 (17)
Cl			
y	0.3804	0.3803 (2)	0.3800 (5)
z	0.2402	0.24020 (8)	0.24037 (17)
b_{11}		0.00661 (8)	0.00643 (23)
b_{22}		0.0312 (4)	0.0320 (12)
b_{33}		0.00660 (8)	0.00643 (23)
b_{23}		-0.00148 (11)	-0.00159 (21)
H			
x	0.3065	Pos. parameters: neutron values used.	
y	0.1295	Thermal parameters: see text.	
z	0.0822		
O			
x	0.2390	0.2402 (3)	0.2408 (4)
b_{11}		0.0042 (2)	0.0036 (3)
b_{22}		0.069 (2)	0.080 (6)
b_{33}		0.0118 (4)	0.0118 (7)
b_{23}		-0.0127 (7)	-0.0148 (17)
Overall scale factor		0.121 (7)	0.122 (36)
R	0.032	0.035	0.047
R_w		0.052	0.057
U		1.02 ($n=548$)	0.96 ($n=225$)

It was realized that the use of spherically symmetrical scattering factors might lead to errors in the thermal vibrational parameters. For Cu and Cl, it could be expected that spherically symmetrical scattering factors would be a good approximation above $\sin\theta/\lambda = 0.50$. For oxygen, however, where most of the electrons take part in the bonding, the scattering factor is still aspherical at higher values of $\sin\theta/\lambda$ (Dawson¹⁷).

Considering the fact that the error introduced by using spherically symmetrical scattering factors would depend on the range of $\sin\theta/\lambda$, it was decided to make refinements with varying lower limit of $\sin\theta/\lambda$ to get an impression of the order of magnitude of the error in the present case. Some of the results are shown in Table 2 and discussed below.

With Cu, Cl, and O in special positions and one of the principal axes of the thermal ellipsoids fixed by symmetry, the number of variable parameters was 16, including anisotropic thermal parameters and an overall scale factor. The hydrogen positions found by Peterson and Levy were generally not varied. The anisotropic vibration parameters of hydrogen were not refined independently, but were set equal to those of oxygen, this being assumed to be a better approximation than isotropic vibration of hydrogen.

The full matrix refinement carried out by means of the ORFLS program by Busing and Levy in the program system X-RAY 63 was followed by the reliability indexes:

$$R = \frac{\sum |F_o - F_c|}{\sum F_o} \quad \text{and} \quad R_w = \sqrt{\frac{\sum w(F_o - F_c)^2}{\sum w F_o^2}}$$

The quantity

$$U = \sqrt{\frac{\sum w(F_o - F_c)^2}{n - p}}$$

and the distribution of $\sqrt{w}(F_o - F_c)$ were used to check the appropriateness of the weighting scheme. (Here, n is the number of independent observations, and p the number of parameters varied.) A system of absolute weights was approached in a way similar to that proposed by Killean.¹⁸ In the present case, a preliminary weighting scheme, yielding a set of approximately correct structure factors F_c' , was based on counting statistics:

$$\frac{1}{w} = \frac{\sigma_{I_o, \text{count}}^2 \cdot \cos\mu}{4 I_o \cdot A \cdot LP} = \sigma_{F_o, \text{count}}^2$$

The distribution of $\sqrt{w}(F_o - F_c')$ thus obtained after four cycles of refinement was slightly skew, and the values of U were about 2.0, indicating underestimation of the standard deviations of some reflexions.

Now, a new weighting scheme was calculated:

$$\frac{1}{w} = \sigma_{F_o, \text{Abs}}^2, \quad \text{where } \sigma_{F_o, \text{Abs}}^2 = \sigma_{F_o, \text{count}}^2 + c^2 F_o'^2$$

Here, the constant c^2 was calculated from

$$\sum (F_o - F_c')^2 = \sum \sigma_{F_o, \text{count}}^2 + c^2 \sum F_o'^2$$

After new refinements using this weighting scheme, the symmetry of the distribution of $\sqrt{w}(F_o - F_c'')$ was improved, and values of U very close to 1 were obtained (Table 2). It should be mentioned that the standard deviations of the parameters after refinement were a trifle greater (but probably more true) with the final than with the preliminary weighting scheme.

Very similar results were obtained using the weighting scheme

$$\sqrt{\frac{1}{w}} = -F_o + \sqrt{\sigma_{F_o}^2 + (1-a)F_o^2}$$

A power series expansion of this expression, using corresponding values of c^2 and a (for example 0.00064, *viz.* 0.05), explains the similarity.

After separate refinements of the data sets hkl and $hkl\bar{}$ it turned out that the resulting parameters were identical within twice the standard deviations in the range $0.50 < \sin \theta/\lambda < 1.00$. The strong reflections suffering from extinction error or counting losses were in the range below $\sin \theta/\lambda = 0.50$; because of this and as a consequence of the possible correlation between thermal parameters and bonding effects at low $\sin \theta/\lambda$, all reflexions below $\sin \theta/\lambda = 0.50$ were excluded from the final refinements. These were based on average values of the hkl and $hkl\bar{}$ data.

To allow for the uncertainty of the Lorentz factor for reflexions near to the rotation axis, reflexions with $\xi < 0.076$ were given zero weight. The same was done to the reflexions in the range $0 < I_o < 2\sigma_{I_o}$.

As a supplement to the least squares refinement, Fourier difference syntheses were calculated by means of the program incorporated in the X-RAY-63-system.

DISCUSSION OF FINAL REFINEMENT RESULTS

Some results of the final refinements are shown in Table 2. For comparison, the parameters found in the neutron work by Peterson and Levy³ are quoted. For chlorine, the parameters found by the neutron and X-ray work are seen to be identical within the standard deviations of the latter. For oxygen, there is a small but not quite negligible difference.

Because of the mutual correlation between the thermal parameters of the atoms, it cannot be expected that refinements with varying lower limit of $\sin \theta/\lambda$ should lead to quite invariable values of the Cu and Cl thermal parameters (assuming spherical scattering to be a good approximation) and varying thermal parameters for oxygen, approaching the true values for $\sin \theta/\lambda \rightarrow 1$. However, inspection of the correlation matrix shows that the correlation terms between the oxygen parameters on one hand, and the scale factor and thermal parameters of the other atoms on the other hand, are comparatively small. Table 2 shows that the changes of the oxygen parameters when the lower limit of $\sin \theta/\lambda$ is shifted are generally greater than those of the other atoms, in good accordance with the assumption that the asphericity is considerable only for oxygen in this range. The trends of the oxygen changes are discussed below.

The final values of R and R_w corresponding to $I_o > 2\sigma_{I_o}$ are shown in Table 2. After refinement, the zero weighted reflexions were checked in the following way. If all of the non-observed reflexions were included in the refinement, inserting $I_o = \sigma_{I_o}$ in the range $0 < I_o < \sigma_{I_o}$ and the true I_o values in the range $\sigma_{I_o} < I_o < 2\sigma_{I_o}$, no changes in the parameters were found; consequently, the R -value of the significantly observed reflexions ($I_o > 2\sigma_{I_o}$) was still 0.035, and for the non-observed reflexions, ($I_o < 2\sigma_{I_o}$), the R -value was 0.068. In this way it was found that 88 % of the I_c values, corresponding to $0 < I_o < \sigma_{I_o}$, were within $0 < I_c < \sigma_{I_o}$ and 100 % within $0 < I_c < 1.7\sigma_{I_o}$. The insertion of $I_o = \sigma_{I_o}$ in the range $0 < I_o < \sigma_{I_o}$ explains the apparent systematic deviation $\text{FOBS} > \text{FCAL}$ of the FOBS values lower than about 1.8 (*cf.* Table 5).

Comparison of the observed and calculated values for the zero weighted reflexions where $\xi < 0.076$ showed that the observed, corrected values were systematically too low.

CALCULATION OF INTERATOMIC DISTANCES, BOND ANGLES, AND ORIENTATION OF THERMAL ELLIPSOIDS

As seen from Table 2, the positional parameters did not change significantly when the lower limit of $\sin\theta/\lambda$ was shifted. As the thermal parameters calculated from high angle reflexions were expected to be nearest to the true

Table 3. Interatomic distances and angles (atom labelling referring to Fig. 1).

	Quoted from neutron work	Neutron param. X-ray cell dim.	Present work $0.80 < \sin\theta/\lambda < 1.0$
Cu(1)–Cl(1d) or (1e)	2.275 Å	2.290 Å	2.290 (4) Å
Cu(1)–Cl(1e, $y+1$)		2.938	2.940 (6)
Cu(1)–O(1d) or (1e)	1.925	1.942	1.957 (5)
O(1d)–Cl(2e)		3.207	3.196 (5)
O(1d)–H(1d) or (1e)	0.948	0.955	0.947
H(1d)–Cl(2e)	2.258	2.261	2.259
H(1d)–H(1e)	1.553	1.564	1.564
\angle Cl(1e)–Cu(1)–Cl(1e, $y+1$)		91.24°	91.19° (19)
\angle Cl(1d)–Cu(1)– <i>c</i> -axis	38°30'	38.70°	38.65° (10)
\angle H(4d)–Cl(1e)–H(5f)		88.14°	88.22°
\angle Cu(2)–Cl(2e)–H(1d)		101.24°	101.29°
\angle O(1d)–H(1d)–Cl(2e)	164°23'	170.68°	169.94°
\angle H(1d)–O(1d)–H(1e)	108°2'	109.91°	111.36°
\angle Cu(1)–O(1d)–H(1d)	125°59'	125.04°	124.32°
\angle HOH–OCuCl (planarity)		179.85°	179.91°

Some distances corrected for thermal motion:

	Independent motion	Riding motion
Cu(1)–Cl(1d) or (1e)	2.308 (4) Å	2.291 (4) Å
Cu(1)–Cl(1e, $y+1$)	2.952 (6)	2.942 (6)
Cu(1)–O(1d) or (1e)	1.990 (5)	1.969 (4)

values, the parameters from the range $0.80 < \sin\theta/\lambda < 1.00$ were used for calculation of the distances and angles of Table 3 and the root mean square displacements and orientations of principal axes of the thermal ellipsoids (Table 4).

To allow for the possible differences between the cell parameters of different crystals, the standard deviations of cell parameters used in Table 3 are twice the values of Table 1.

Peterson and Levy³ do not specify the values of cell parameters they use for the calculation of angles and bond lengths. For comparison with the values of the present work, the neutron positional parameters are combined with the cell parameters of the present work in column 2 of Table 3. This recalculation led to considerable changes, especially as far as the angles are concerned.

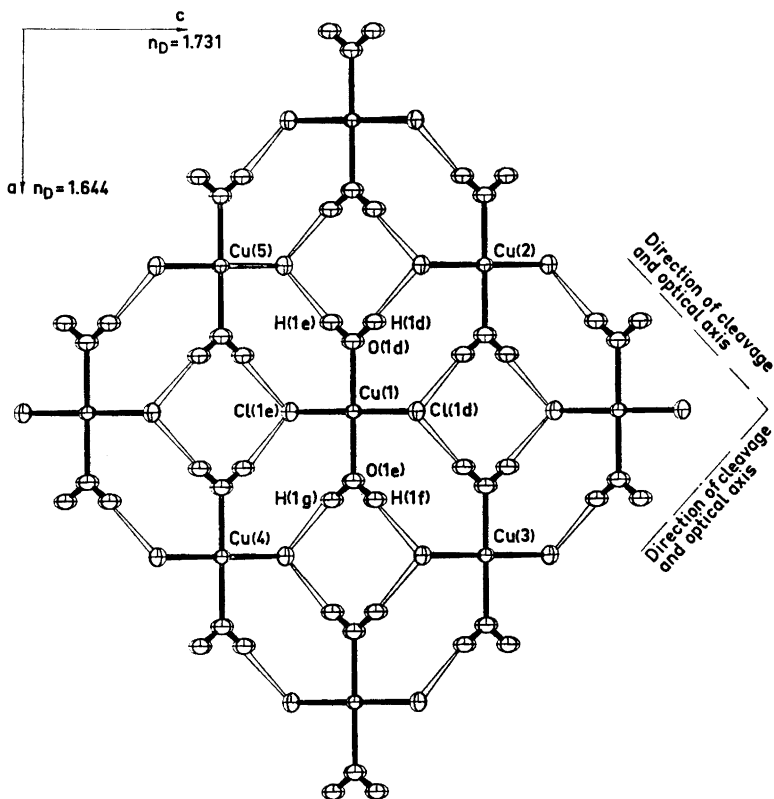


Fig. 1. Bond direction and vibrational ellipsoids in a cross section corresponding to the normal crystal habit. The unit cell is limited by the copper atoms labelled 2, 3, 4, and 5. The lattice is built up from layers of the kind shown here, translated 3.76 Å with respect to each other in the direction of the *b* axis. While the thermal ellipsoids of Cu, Cl, and O of Figs. 1 and 2 are results of the present work, those shown for H are only proposals.

DISCUSSION OF THE STRUCTURE

The main feature of the structure is columns of planar $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ molecules stacked in the length direction of the crystal (b -axis). The planar molecules are parallel to each other within a single column. Further, they are parallel to the a -axis and tilted 51.3° with respect to the b -axis. Each column is centering a square of 4 other columns with opposite tilt of the molecules (Figs. 1 and 2).

The columns are connected to each other by means of hydrogen bonds $\text{O}-\text{H} \cdots \text{Cl}$, each Cl being the acceptor of two hydrogen bonds nearly at right angles to each other. Thus, each molecule is linked to 4 other molecules in neighbouring columns by a total of 8 hydrogen bonds.

The bond lengths $\text{O}-\text{H}$ (0.947 Å) and $\text{H}-\text{Cl}$ (2.259 Å) are very usual. In accordance with the experiences of other authors (Hamilton and Ibers¹⁹), an attempt to refine the hydrogen position by the least squares method led to a considerably shorter $\text{O}-\text{H}$ bond (0.87 Å). At the same time, the water angle was increased (133°) and the water molecule was found to form an angle of 13° with the $\text{Cu}-\text{Cl}-\text{O}$ plane. These values were not found to be trustworthy, and the distances and angles of Table 3 are based on insertion of the neutron hydrogen parameters.

The configuration and bond lengths around the copper atom have been discussed by Wells¹⁰ and Harker.¹ Here, it should only be mentioned that the line connecting the two long-distance chlorine atoms ($\text{Cu}-\text{Cl}=2.940$ Å) in the Jahn-Teller distorted octahedron around Cu is forming an angle of 91.19° with the square plane formed by two $\text{Cu}-\text{O}$ and two short $\text{Cu}-\text{Cl}$ bonds ($\text{Cu}-\text{Cl}=2.290$ Å).

The $\text{H}-\text{O}-\text{H}$ angle of 111.36° indicates sp^3 hybridization with some sp^2 character. This point is discussed by Hamilton and Ibers,¹⁹ who call attention to the tendency of the transition metal hydrates to form big water angles ($\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ 115° ; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 109°).

The calculation of scattering factors for oxygen assuming sp^2 or sp^3 hybrid orbitals has been treated by Dawson.¹⁷ For corresponding orientation of the orbital axes, the differences between the scattering factors of the sp^2 and sp^3 hybrids are small.

In the present case, using Dawson's notation, the z hybrid axis (bisecting the angle between the two lone pair orbitals) is along the $\text{Cu}-\text{O}$ bond, *i.e.* parallel to the a -axis. Assuming that the direction of the x -orbital axis is parallel to the $\text{H}-\text{H}$ vector, the direction of the y -orbital axis is also fixed. Consequently, in the present case it is rather simple to derive the expression for the aspherical scattering factor and the structure factor sum for the two oxygen atoms in $(x,0,0)$ and $(-x,0,0)$:

$$F_{\text{O},\pm} = 2[(f_1'' \cdot p^2 + f_2'' \cdot q^2 + f_3'' \cdot r^2) \cos 2\pi hx - f_a'' \cdot r \cdot \sin 2\pi hx] \exp[-(b_{11}h^2 + \dots)]$$

where f_1'' , f_2'' , f_3'' and f_a'' , all dependent on $\sin\theta/\lambda$, are calculated by Dawson,¹⁷ and p, q , and r are the direction cosines of the scattering vector with respect to the hybrid orbital coordinate system.

At the present time, a least squares program for the refinement based on these aspherical scattering factors is not at the author's disposal. However,

a qualitative comparison with Dawson's calculations of the change of positional and thermal parameters for N in the sp^3 hybrid state (compared with the "spherical state") is interesting:

Dawson finds that least squares refinement using spherical scattering factors leads to positional displacement towards the lone pair, *i.e.* along the z hybrid axis. In the oxygen case of the present work, the positional parameter is also shifted toward the lone pairs along the z hybrid axis, when the lower limit of $\sin\theta/\lambda$ is changed from 0.80 to 0.50, *i.e.* when the error introduced by the use of spherically symmetrical scattering factors is increased. At the same time, the thermal parameter b_{11} corresponding to the same direction is increased, and b_{22} is decreased, also consistent with the results found by Dawson.

It should be mentioned that for reflexions above $\sin\theta/\lambda = 0.80$, the anti-symmetrical term f_a'' is small. The absence of the term f_a'' in the structure factor calculation for oxygen in the present case shows up in the Fourier difference synthesis in the following way ($0.50 < \sin\theta/\lambda < 1.00$): Along the z -hybrid axis (crystallographic a -axis), a minimum of $0.3 \text{ e}/\text{Å}^3$ is found with its center about 0.12 Å away from the oxygen position towards the copper atom. In the opposite direction, a zero line intersects the z -hybrid axis at a distance of 0.3 Å from the oxygen atom, and a weak maximum, $0.2 \text{ e}/\text{Å}^3$ is found centered around a point 0.55 Å from the oxygen position.

In the corresponding difference synthesis for the range $0.80 < \sin\theta/\lambda < 1.00$, the minimum has disappeared, and the maximum is reduced to $0.1 \text{ e}/\text{Å}^3$.

DISCUSSION OF THERMAL VIBRATIONS: DERIVATION OF THE STRUCTURE OF ANHYDROUS COPPER CHLORIDE

In agreement with the expectations mentioned in the introduction, the vibration of the oxygen atoms is really found to be anisotropic. The largest root mean square displacement is about twice as great as the mean of the r.m.s. displacements in the directions perpendicular to it.

Table 4. Orientation of thermal ellipsoid axes and r.m.s. displacement along these axes ($\sin\theta/\lambda > 0.80$).

	Ellips. axis	r.m.s. displacement	Angle with cryst. axis		
			<i>a</i>	<i>b</i>	<i>c</i>
Cu	1	0.112 (3) Å	0°	90.0°	90.0°
	2	0.121 (3) Å	90.0°	52.8(1.3)	37.2(1.3)
	3	0.162 (2) Å	90.0°	37.2(1.3)	52.8(1.3)
O	1	0.110 (5) Å	0.0	90.0	90.0
	2	0.145 (5) Å	90.0	60.1(2.2)	29.9(2.2)
	3	0.263 (10) Å	90.0	29.9(2.2)	60.1(2.2)
Cl	1	0.131 (3) Å	90.0	68.9(2.7)	21.1(2.7)
	2	0.147 (2) Å	0.0	90.0	90.0
	3	0.155 (3) Å	90.0	21.1(2.7)	68.9(2.7)

As seen from Fig. 2 and Table 4, there seems to be some correlation between the vibrations of copper and oxygen. However, while the largest displacement of the copper atom is in the direction nearly perpendicular (deviation $1.45 \pm 1.3^\circ$) to the plane of the molecule, the largest axis of the oxygen vibration ellipsoid is turned 8° towards the *b*-axis, referring to the largest copper ellipsoid axis. The angle between the length direction of the crystal (*b*-axis) and the direction of largest vibration of the oxygen atom is 29.9° .

The vibrational ellipsoid of the chlorine atom is not far from being a rotational ellipsoid, the axis of rotation (corresponding to the smallest displacement) forming an angle of 68.9° with the *b*-axis. Thus, the vibration of the Cl-atom seems to be rather independent of the copper and oxygen vibrations.

The Cu—O and the two Cu—Cl distances are corrected for thermal motion using both the riding motion model and the independent motion model, and the results are shown in Table 3. As a consequence of the above-mentioned remarks, the riding motion is assumed to be most probable for the Cu—O bond and the independent motion for the Cu—Cl bonds.

The vibration pattern found for the oxygen atoms together with the kinetic measurements (Engberg ⁴) support the assumption that the dehydration takes place through successive jumps of the water molecules in the length direction of the crystal. Direct observation of a copper chloride dihydrate crystal during dehydration on a hot stage demonstrates the formation of long, light brown domains of anhydrous copper chloride, as the dehydration propagates in the direction of the *b*-axis.

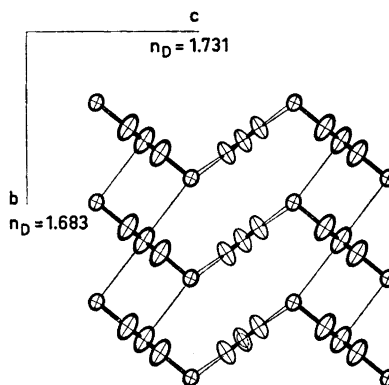
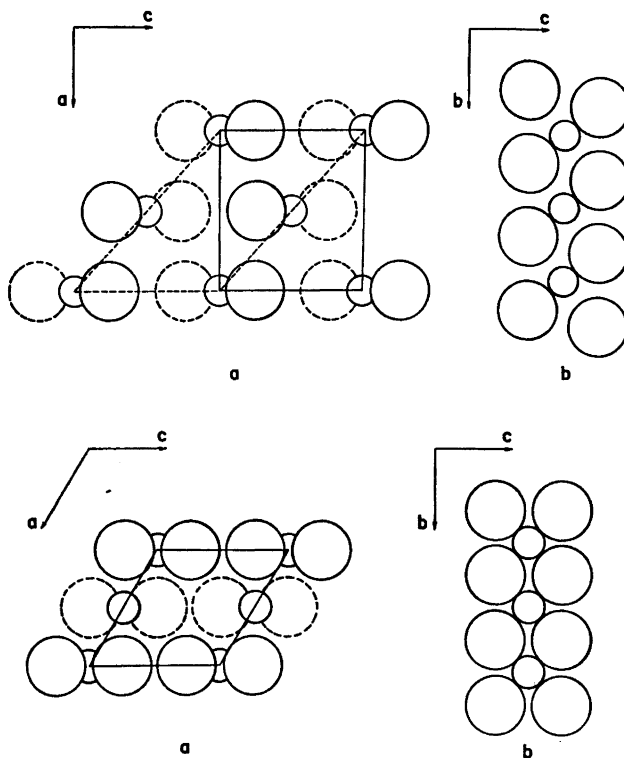


Fig. 2. Thermal vibrations in three adjacent columns, the top molecules corresponding to those centered by Cu(4), Cu(1), and Cu(3) of Fig. 1. The copper atoms are hidden behind the oxygen atoms, but the conformity of the vibrations of the two kinds of atoms is indicated by the dotted copper ellipsoid shown in one of the oxygen ellipsoids. The single lines denote the long Cu—Cl bonds completing the distorted octahedral configuration around the copper atoms.

The structure of anhydrous copper chloride may be derived from the dihydrate structure as follows: The columns of copper chloride dihydrate molecules may also be regarded as chains of slightly distorted octahedrons, each sharing 2 opposite edges with the neighbours in the chain. By removal of the water molecules, chains of square planar coordinated copper atoms with two different Cu—Cl distances are left back (Fig. 3b). A slight rearrangement leads to chains of the kind found by Wells ¹⁰ in the anhydrous structure (Fig. 4b), where all Cu—Cl-distances are equal.



Figs. 3 and 4. Comparison of the structures of the dihydrate and the anhydrous copper chloride. Figs. 3a and b show the dihydrate structure after removal of the water molecules, *i.e.* a unit cell (limited by full lines in Fig. 3a), the expanded monoclinic cell of the anhydrous copper chloride (limited by dotted lines), and a CuCl_2 chain. Figs. 4a and b show the true monoclinic cell and a CuCl_2 chain of the anhydrous copper chloride.

Further, a rearrangement of the chains with respect to each other is necessary. By comparison of Figs. 3a and 4a, it is seen how the expanded monoclinic unit cell of the anhydrous structure is contained in the structure of the dihydrate.

HABIT AND OPTICAL PROPERTIES CORRELATED TO THE STRUCTURE

In good accordance with the structure as shown in Figs. 1 and 2, the great majority of crystals are prisms elongated in the *b*-axis direction and with well developed faces 101. The habit reflects the structure of columns held together by hydrogen bonds; the relative weakness of these bonds often leads to disorder in the arrangement of the columns, resulting in a slight deviation of the angles between faces compared to the theoretical angles corresponding to 101. Such crystals produced multiple spots on the Weissenberg films. The kind of

Table 5. Observed and calculated structure factors, 100 times absolute values. Reflexions where $I_0 < 2\sigma I_0$ are denoted by an L. Range $0.50 < \sin\theta/\lambda < 1.00$.

h	k	l	FOBS	FCAL	h	k	l	FOBS	FCAL	h	k	l	FOBS	FCAL	h	k	l	FOBS	FCAL
0	0	8	3526	3690	2	1	13	302	259	12	1	3	538	557	7	2	7	896	877
0	0	10	263	232	2	1	14	501	531	12	1	4	606	578	7	2	8	417	362
0	0	12	1432	1370	3	1	7	2283	2276	12	1	5	358	370	7	2	9	729	748
1	0	9	2157	2137	3	1	8	561	585	12	1	6	1254	1273	7	2	10	392	454
1	0	11	321	199	3	1	9	571	576	12	1	7	387	378	7	2	11	422	427
1	0	13	975	963	3	1	10	289	349	12	1	8	371	394	8	2	0	229	2228
2	0	8	2733	2787	3	1	11	1137	1147	12	1	9	347	164	8	2	1	1631	1637
2	0	10	244	194	3	1	12	375	365	13	1	1	1062	1049	8	2	2	1917	1919
2	0	12	1147	1102	3	1	13	L 1874	165	13	1	2	L 198	29	8	2	3	1290	1282
2	0	14	L 190	45	4	1	7	1274	1274	13	1	3	1033	1075	8	2	4	1779	1705
3	0	7	958	947	4	1	8	752	708	13	1	4	L 183	127	8	2	5	1383	1351
3	0	9	1921	1919	4	1	9	643	615	13	1	5	704	725	8	2	6	1300	1280
3	0	11	L 172	168	4	1	10	1679	1675	13	1	6	L 190	57	8	2	7	697	700
4	0	8	3067	3157	4	1	11	531	560	13	1	7	754	799	8	2	8	1037	1002
4	0	13	938	889	4	1	12	351	324	13	1	8	L 188	157	8	2	9	797	744
4	0	10	L 237	230	5	1	6	245	318	14	1	0	L 182	218	8	2	10	669	669
4	0	12	1220	1208	5	1	7	2164	2156	14	1	1	362	341	8	2	11	329	235
4	0	14	266	158	5	1	8	337	519	14	1	2	897	923	9	2	1	1675	1663
5	0	7	1055	1047	6	1	9	525	631	14	1	3	324	319	9	2	2	L 209	233
5	0	9	1792	1788	5	1	10	289	281	14	1	4	L 198	216	9	2	3	1483	1465
5	0	11	L 229	239	5	1	11	1072	1076	14	1	5	L 258	248	9	2	4	L 215	165
5	0	13	806	825	5	1	12	347	328	14	1	6	696	686	9	2	5	1325	1284
6	0	6	395	351	6	1	5	1239	1212	15	1	1	455	448	9	2	6	474	466
6	0	8	2047	2073	6	1	6	2303	2332	15	1	2	209	26	9	2	7	905	898
6	0	10	L 171	83	6	1	7	942	933	15	1	3	511	490	9	2	8	L 178	199
6	0	12	875	864	6	1	8	L 186	97	15	1	4	1330	1395	9	2	9	734	758
7	0	5	2044	2061	6	1	9	565	595	0	2	8	1709	1682	9	2	10	404	389
7	0	7	603	590	6	1	10	1140	1122	0	2	9	1363	1362	9	2	11	459	446
7	0	9	1303	1318	6	1	11	409	404	0	2	10	990	1028	10	2	0	1005	1025
7	0	11	L 180	158	6	1	12	L 207	139	0	2	11	453	474	10	2	1	1127	1111
7	0	13	622	652	6	1	13	208	188	0	2	12	618	661	10	2	2	895	844
8	0	2	807	799	7	1	4	279	309	0	2	13	448	503	10	2	3	1007	997
8	0	4	3604	3787	7	1	5	1116	1085	0	2	14	388	417	10	2	4	839	860
8	0	6	427	446	7	1	6	318	298	1	2	7	1493	1509	10	2	5	836	849
8	0	8	2044	2057	7	1	7	1476	1500	1	2	8	551	541	10	2	6	654	629
8	0	10	L 211	242	7	1	8	329	385	1	2	9	1214	1181	10	2	7	614	582
8	0	12	908	847	7	1	9	381	412	1	2	10	755	744	10	2	8	529	541
9	0	1	2174	2221	7	1	10	302	241	1	2	11	577	625	10	2	9	460	456
9	0	3	1642	1623	7	1	11	813	823	1	2	12	349	336	10	2	10	332	384
9	0	5	1886	1914	8	1	0	1293	1260	1	2	13	497	503	11	2	1	869	867
9	0	7	737	743	8	1	1	1222	1196	2	2	7	1518	1527	11	2	2	L 163	126
9	0	9	1159	1188	8	1	2	3579	3725	2	2	8	1087	1037	11	2	3	773	775
9	0	11	L 251	264	8	1	3	1212	1224	2	2	9	1101	1107	11	2	4	L 194	157
10	0	0	2425	2502	8	1	4	1604	971	2	2	10	639	652	11	2	5	689	715
10	0	2	259	193	8	1	5	842	815	2	2	11	597	588	11	2	6	L 224	262
10	0	4	2060	2060	8	1	6	2410	2435	2	2	12	454	449	11	2	7	478	514
10	0	6	L 165	92	8	1	7	795	797	2	2	13	325	403	11	2	8	L 182	183
10	0	8	1208	1219	8	1	8	527	526	3	2	6	819	821	11	2	9	444	457
10	0	10	185	57	8	1	9	337	380	3	2	7	1305	1313	12	2	0	1128	1145
11	0	1	1104	1077	8	1	10	1164	1149	3	2	8	545	574	12	2	1	731	749
11	0	3	728	733	8	1	11	436	361	3	2	9	1078	1058	12	2	2	1010	1008
11	0	5	1047	1061	8	1	12	243	286	3	2	10	700	676	12	2	3	590	587
11	0	7	395	367	9	1	1	1902	1916	3	2	11	556	564	12	2	4	956	968
11	0	9	737	743	9	1	2	L 154	79	3	2	12	290	321	12	2	5	627	633
12	0	0	2204	2233	9	1	3	1938	1979	3	2	13	446	462	12	2	6	761	743
12	0	2	425	458	9	1	4	247	275	4	2	6	1995	1976	12	2	7	275	303
12	0	4	1858	1860	9	1	5	1198	1174	4	2	7	1144	1126	12	2	8	584	607
12	0	6	374	356	9	1	6	L 262	172	4	2	8	1485	1456	13	2	1	921	932
12	0	8	1137	1103	9	1	7	L 1372	1393	4	2	9	1180	1165	13	2	2	L 185	104
13	0	1	1187	1179	9	1	8	368	322	4	2	10	932	914	13	2	3	821	845
13	0	3	952	926	9	1	9	533	515	4	2	11	414	399	13	2	4	L 184	50
13	0	5	996	1043	9	1	10	L 189	145	4	2	12	608	599	13	2	5	793	758
13	0	7	513	525	9	1	11	700	751	4	2	13	326	439	13	2	6	L 201	229
14	0	0	1145	1140	10	1	0	361	154	5	2	5	2013	1995	13	2	7	585	570
14	0	2	L 181	83	10	1	1	914	874	5	2	6	781	758	14	2	0	511	561
14	0	4	981	975	10	1	2	1927	1959	5	2	7	1276	1284	14	2	1	440	443
14	0	6	L 190	118	10	1	3	801	790	5	2	8	345	404	14	2	2	471	490
15	0	1	448	503	10	1	4	L 196	140	5	2	9	1045	1026	14	2	3	372	385
15	0	3	335	387	10	1	5	656	644	5	2	10	603	613	14	2	4	457	493
0	1	8	818	821	10	1	6	1371	1348	5	2	11	497	570	14	2	5	348	349
0	1	9	736	714	10	1	7	548	505	5	2	12	279	247	15	2	1	418	431
0	1	10	1954	1921	10	1	8	176	159	5	2	13	421	453	15	2	2	L 233	45
0	1	11	571	651	10	1	9	316	311	6	2	4	1484	1439	0	3	6	740	772
0	1	12	359	359	10	1	10	691	706	6	2	5	1589	1570	0	3	7	1309	1321
0	1	13	L 212	219	10	1	11	L 250	226	6	2	6	998	983	0	3	8	1955	1954
0	1	14	654	658	11	1	1	916	921	6	2	7	1108	1104	0	3	9	325	360
1	1	8	643	640	11	1	2	L 166	69	6	2	8	799	813	0	3	10	390	360
1	1	9	688	677	11	1	3	1032	1032	6	2	9	788	823	0	3	11	621	608
1	1	10	L 229	371	11	1	4	L 165	158	6	2	10	530	535	0	3	12	777	830
1	1	11	1293	1257	11	1	5	606	583	6	2	11	464	423	1	3	5	1952	1992
1	1	12	400	400	11	1	6	234	151	6	2	12	355	381	1	3	6	311	289
2	1	7	1256	1262	11	1	7	808	820	7	2	1	1753	1729	1	3	7	909	904
2	1	9																	

Table 5. Continued.

h	k	l	FOBS	FCAL	h	k	l	FOBS	FCAL	h	k	l	FOBS	FCAL	h	k	l	FOBS	FCAL			
1	3	13	503	542	10	3	1	651	675	4	4	9	307	268	1	5	7	297	295			
2	3	5	1213	1219	10	3	2	228	197	4	4	10	1024	992	1	5	8	L	172	45		
2	3	6	198	114	10	3	3	634	639	5	4	1	1167	1190	1	5	9		678	674		
2	3	7	1025	1025	10	3	4	1157	1133	5	4	2	183	139	1	5	10		307	243		
2	3	8	1465	1467	10	3	5	476	465	5	4	3	1362	1366	2	5	0	1506	1653			
2	3	9	554	548	10	3	6	196	176	5	4	4	248	62	2	5	1	591	652			
2	3	10	L	220	89	10	3	7	423	454	5	4	5	601	652	2	5	2	134	117		
2	3	11	457	444	10	3	8	716	708	5	4	6	253	285	2	5	3	516	526			
2	3	12	636	647	11	3	1	708	723	5	4	7	1102	1079	2	5	4	1336	1363			
3	3	4	567	524	11	3	2	L	169	52	5	4	8	L	150	80	2	5	5	253	566	
3	3	5	1765	1764	11	3	3	580	584	5	4	9	235	260	2	5	6	L	563	566		
3	3	6	332	293	11	3	4	L	204	169	5	4	10	260	245	2	5	7	223	285		
3	3	7	779	797	11	3	5	632	660	5	4	11	678	641	2	5	8		817	796		
3	3	8	596	621	11	3	6	L	174	108	6	4	0	369	299	2	5	9	320	359		
3	3	9	1079	1027	11	3	7	323	360	6	4	1	L	153	170	2	5	10	L	155	58	
3	3	10	295	239	11	3	8	310	210	6	4	2	2023	2009	3	5	1	844	878			
3	3	11	313	308	12	3	0	1277	1225	6	4	3	129	88	3	5	2	145	110			
3	3	12	432	398	12	3	1	369	417	6	4	4	216	231	3	5	3	571	588			
4	3	3	1625	1619	12	3	2	446	468	6	4	5	L	173	165	3	5	4	L	117	25	
4	3	4	2996	3046	12	3	3	474	479	6	4	6	1424	1394	3	5	5	889	876			
4	3	5	881	853	12	3	4	1089	1044	6	4	7	L	152	16	3	5	6	259	236		
4	3	6	654	660	12	3	5	L	179	230	6	4	8	L	154	79	3	5	7	284	267	
4	3	7	1141	1139	12	3	6	385	370	6	4	9	L	158	107	3	5	8	L	151	31	
4	3	8	1733	1700	12	3	7	394	365	6	4	10	715	710	3	5	9	649	622			
4	3	9	316	302	13	3	1	735	741	7	4	1	863	837	4	5	0	1617	1707			
4	3	10	293	344	13	3	2	L	179	2	7	4	2	L	137	87	4	5	1	589	609	
4	3	11	526	531	13	3	3	648	639	7	4	3	1030	1000	4	5	2	202	128			
4	3	12	748	744	13	3	4	L	183	163	7	4	4	L	188	13	4	5	3	395	389	
5	3	2	2018	2026	13	3	5	653	656	7	4	5	459	463	4	5	4	1393	1430			
5	3	3	L	71	14	3	0	694	678	7	4	6	L	216	186	4	5	5	595	613		
5	3	4	1602	1578	14	3	1	L	237	264	7	4	7	816	822	4	5	6	L	172	158	
5	3	5	516	512	14	3	2	L	178	222	7	4	8	L	157	27	4	5	7	L	139	138
5	3	6	1645	1652	14	3	3	266	265	7	4	9	L	157	188	4	5	8	870	868		
5	3	7	236	200	0	4	1	106	296	8	4	0	L	136	125	4	5	9	434	426		
5	3	8	830	803	0	4	2	3108	3339	8	4	1	209	161	4	5	10	L	197	172		
5	3	9	573	578	0	4	3	L	95	20	8	4	2	1888	1867	5	5	1	820	832		
5	3	10	1000	980	0	4	4	L	100	71	8	4	3	L	149	18	5	5	2	L	139	106
5	3	11	L	220	162	0	4	5	418	421	8	4	4	L	159	128	5	5	3	585	579	
5	3	12	309	339	0	4	6	2199	2271	8	4	5	L	188	241	5	5	4	L	154	44	
6	3	0	335	375	0	4	7	L	195	204	8	4	6	1342	1322	5	5	5	841	820		
6	3	1	2402	2329	0	4	8	L	158	82	8	4	7	L	200	136	6	5	6	229	234	
6	3	2	1265	1265	0	4	9	333	300	8	4	8	L	226	149	5	5	7	238	292		
6	3	3	219	196	0	4	10	1118	1121	9	4	1	811	812	5	5	8	L	155	61		
6	3	4	1204	1179	1	4	1	1323	1413	9	4	2	201	94	5	5	9	596	588			
6	3	5	1985	1929	1	4	2	189	161	9	4	3	954	921	6	5	0	1259	1257			
6	3	6	871	886	1	4	3	1610	1632	9	4	4	L	151	63	6	5	1	496	480		
6	3	7	L	161	136	1	4	4	L	110	52	9	4	5	477	509	6	5	2	L	119	37
6	3	8	747	755	1	4	5	717	725	9	4	6	L	202	202	6	5	3	429	378		
6	3	9	1126	1132	1	4	6	281	325	9	4	7	732	749	6	5	4	1071	1050			
6	3	10	412	389	1	4	7	1278	1267	9	4	8	L	164	86	6	5	5	424	425		
6	3	11	167	118	1	4	8	169	62	10	4	0	L	196	62	6	5	6	196	22		
6	3	12	304	337	1	4	9	255	243	10	4	1	L	155	94	6	5	7	211	198		
7	3	0	532	520	1	4	10	288	272	10	4	2	1220	1176	6	5	8	674	631			
7	3	1	1352	1332	1	4	11	754	739	10	4	3	L	159	39	6	5	9	250	277		
7	3	2	L	129	108	2	4	0	435	439	10	4	4	L	154	26	7	5	1	652	637	
7	3	3	1065	1040	2	4	1	247	230	10	4	5	L	193	102	7	5	2	L	127	74	
7	3	4	295	341	2	4	2	2603	2699	10	4	6	867	847	7	5	3	400	442			
7	3	5	1175	1175	2	4	3	L	106	128	10	4	7	L	181	26	7	5	4	142	17	
7	3	6	254	214	2	4	4	405	383	11	4	1	559	501	7	5	5	668	639			
7	3	7	599	560	2	4	5	237	211	11	4	2	L	167	44	7	5	6	L	147	163	
7	3	8	437	412	2	4	6	1843	1827	11	4	3	616	581	7	5	7	L	180	225		
7	3	9	739	737	2	4	7	L	143	6	11	4	4	L	162	8	7	5	8	L	158	27
7	3	10	L	171	164	2	4	8	205	180	11	4	5	312	313	8	5	0	1159	1153		
7	3	11	232	252	2	4	9	L	152	130	11	4	6	L	175	98	8	5	1	414	385	
8	3	0	2404	2358	2	4	10	950	901	12	4	0	L	215	192	8	5	2	L	136	163	
8	3	1	888	914	2	4	11	L	175	76	12	4	1	L	170	79	8	5	3	256	234	
8	3	2	685	703	2	4	12	L	178	6	12	4	2	1025	998	8	5	4	1030	979		
8	3	3	1027	1018	3	4	1	1184	1230	12	4	3	L	172	23	8	5	5	393	403		
8	3	4	1984	1947	3	4	2	185	136	12	4	4	L	210	189	8	5	6	L	151	176	
8	3	5	513	526	3	4	3	1457	1458	12	4	5	279	135	8	5	7	L	196	65		
8	3	6	476	491	3	4	4	L	130	31	13	4	1	499	510	9	5	1	615	591		
8	3	7	750	729	3	4	5	642	642	0	5	1	366	712	9	5	2	L	145	75		
8	3	8	1179	1160	3	4	6	260	283	0	5	2	114	117	9	5	3	496	443			
8	3	9	L	245	168	3	4	7	1178	1154	0	5	4	1582	1638	9	5	4	L	156	49	
8	3	10	285	303	3	4	8	L	144	41	0	5	5	695	709	9	5	5	587	581		
8	3	11	389	359	3	4	9	294	214	0	5	6	L	124	149	9	5	6	L	195	167	
9	3	1	1299	1272	3	4	10	L	199	238	0	5	7	L	142	172	10	5	0	770	767	
9	3	2	L	162	38	3	4	11	672	679	0	5	8	1018	977	10	5	1	301	262		
9	3	3	1044	1038	4	4	0	L	102	87	0	5	9	423	483	10	5	2	L	149	68	
9	3	4	285	317	4	4	1	242	235	0	5	10	237	174	10	5	3	L	198	195		
9	3	5	1081	1105	4	4	2	2764	2862	1	5	1	869	969	10	5	4	639	654			
9	3	6	L	161	80	4	4	3	L	113</												

disorder might explain the deviations between the cell dimensions of different crystals mentioned earlier. The point is discussed in general by Lonsdale.²⁰

According to Neuhaus,²¹ the main indices of refraction for Na_D are $n_\alpha = 1.644 \pm 0.002$, $n_\beta = 1.683 \pm 0.002$, and $n_\gamma = 1.731 \pm 0.002$. By immersion in α -monobromonaphthalene, $n_D = 1.659$, the main indices could be associated to the structure as shown in Figs. 1 and 2. As the polarizability in the Cu–Cl-direction would be expected to be greater than in the Cu–O direction, the result is not surprising.

The plane of the optical axes is perpendicular to the length direction of the crystal. The acute axial angle is calculated to be 86.26° for Na_D . The acute angle between 101 faces is 84.96° , *i.e.* close to the optical axial angle. For crystals lying on 101 faces, one of the optical axes was nearly perpendicular to the stage of the microscope. Consequently, the directions of the optical axes for Na_D are nearly parallel to the faces 101, as shown in Fig. 1.

It is notable that all Cu–O bonds are parallel to the *a*-axis. Bearing in mind the shift of colour from blue to yellow when H_2O is replaced by Cl^- as ligand for Cu^{2+} in solution, pleochroism could be expected, when the plane of vibration of white light was turned from the direction parallel to Cu–O to the direction perpendicular to this bond. For crystals lying on 101 faces, pleochroism is difficult to detect, the Cu–O bonds forming an angle of 42.5° with the stage. However, twins with twin plane 210 were rather common, consisting of two branches at right angles to each other, and lying with the *c*-axis perpendicular to the stage. Here, the colour was bluish in the branch where the *a*-axis, *i.e.* the Cu–O bonds, were parallel to the direction of vibration of the light, and greenish in the other branch.

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