

The crystal structure of buttgenbachite

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SUMMARY. The crystal structure of buttgenbachite from Likasi (Congo) was solved by a three-dimensional Patterson function, computed using intensity data collected photographically by the Weissenberg method, and refined by successive Fourier maps and least-squares refinement to an R index 0.055 for 328 independent observed reflections. The cell content resulting from the structural analysis is $\text{Cu}_{3.6}\text{Cl}_{6.7}(\text{NO}_3)_{2.6}(\text{OH})_{63.9} \cdot 2.1 \text{H}_2\text{O}$. The space group is $P6_3/mmc$ with $a = 15.750 \text{ \AA}$ and $c = 9.161 \text{ \AA}$. The buttgenbachite structure is not completely ordered. It consists of a rigid three-dimensional skeleton formed by Cu co-ordination polyhedra sharing edges and corners. The large channels in the framework show a zeolite-like nature; inside the channels the disorder is caused by the different orientations of nitrate groups and by the occurrence of the substitution $2\text{NO}_3^- \rightleftharpoons \text{Cl}^-$. The crystal structure of buttgenbachite is closely related to that of connellite. The mechanism of forming an isomorphous series is discussed: the present study shows that the replacement is more complicated than was supposed in the literature.

BUTTGENBACHITE is a basic copper nitrate-chloride discovered by Schoep (1925) at Likasi (Congo). The mineral occurs as aggregates of fine azure-blue needles with elongation [0001]. The chemical formula suggested by Bannister *et al.* (1950) is $\text{Cu}_{19}\text{Cl}_4(\text{NO}_3)_2(\text{OH})_{32} \cdot X \text{H}_2\text{O}$ (with $X = 2$ or 3). The specific density measured by Schoep is 3.33 g cm^{-3} and that measured by Bannister *et al.* is 3.42 g cm^{-3} . The space groups proposed by these authors on the basis of systematic absences are $P6_3mc$, $P\bar{6}2c$, and $P6_3/mmc$.

Buttgenbachite is closely related to connellite, which is a hydrated basic chloride-sulphate of copper. X-ray investigations by Bannister *et al.* suggest the existence of an isomorphous series. This agrees with the occurrence of intermediate compounds at Likasi, as indicated by Buttgenbach (1926), where SO_4^{2-} and NO_3^- apparently substitute mutually. In order to explain how this replacement can occur from a structural point of view, we undertook the crystal structure of buttgenbachite. The preliminary results of this study were discussed during the 5th Meeting of the Italian Crystallography Association in Bari (Fanfani *et al.*, 1971). The recent crystal structure determination of connellite (McLean and Anthony, 1972) permits an interesting comparison of the results concerning these minerals.

Experimental. An acicular crystal of a sample of buttgenbachite from the type locality of Likasi was chosen for X-ray study and mounted with [0001] (the elongation direction) as rotation axis. Weissenberg integrated photographs of $h \cdot k \cdot h + k \cdot 0$ levels of the reciprocal lattice were recorded employing Cu- $K\alpha$ radiation. A total of 328 independent reflections with intensity above the limit of observation were evaluated

with the aid of a microdensitometer, while 315 reflections were too weak to be observed. The intensities were put on the same approximate scale by means of the common reflections collected on a $ok\bar{k}l$ Weissenberg photograph obtained with a different mounting of the crystal. The unit cell constants of buttggenbachite, refined with data from basal Weissenberg photographs, are $a = 15.750 \pm 0.003 \text{ \AA}$, $c = 9.161 \pm 0.002 \text{ \AA}$.

The centric space group $P6_3/mmc$ was assumed at the beginning of the study, taking into account the lack of pyroelectricity in the mineral (Miers, 1894).

Because of the small amount of material available, it was impossible to perform a quantitative determination of the elements. A spectrographic analysis on the small crystal employed in collecting X-ray data was carried out by means of a laser microprobe. This analysis enabled us to determine that aluminium is present in buttggenbachite in a concentration higher than 0.1 %. However, because of the impossibility of determining the chemical formula more exactly, at the beginning of our study we assumed the cell content proposed by Bannister *et al.*, $2\text{Cu}_{1.9}\text{Cl}_4(\text{NO}_3)_2(\text{OH})_{3.2} \cdot 2\text{H}_2\text{O}$. The corresponding specific density is 3.46 g cm^{-3} .

The usual geometrical corrections were applied to the intensity data, while absorption corrections were neglected in view of the small dimensions of the crystal ($0.01 \times 0.03 \times 0.27 \text{ mm}$; $\mu = 140 \text{ cm}^{-1}$). A three-dimensional Patterson function was computed and its interpretation in the centric space group allowed us to locate 36 Cu ions in the unit-cell. Successive Fourier syntheses showed the atomic arrangement around these Cu ions. At this stage 36 Cu, 6 Cl, and 66 O atoms were located in the unit cell. From a difference Fourier synthesis a high residual electronic density was observed at the inversion centre 0,0,0 and at different positions on the \bar{b} axis and around it at distances corresponding to N–O bonds. From this it was concluded that the crystal structure of buttggenbachite is partially disordered and the nature of disorder is such that a completely ordered atomic arrangement cannot be obtained even if the two less symmetrical space groups are considered.

The two-fold site at the origin of the cell was supposed to be randomly occupied by Cu atoms, on the basis of the lower content of copper found in the unit-cell with respect to the proposed chemical formula. The atom appears to be six-coordinated to six equivalent oxygen atoms. In this site we suppose that a certain amount of aluminium, as revealed by the spectrographic analysis, is located. However, during the structural analysis the scattering factor curve of Cu atom was employed for the position 0,0,0 and the occupancy was refined on the basis that only Cu atoms were present in that position. Their occupancy is about one-third the maximum.

Along the \bar{b} axis the six-fold position $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$ with symmetry $\bar{6}m2$ was supposed to be occupied with occupancy less than half the maximum by a Cl^- ion, while two NO_3^- groups from opposite sides of the Cl^- ion were inferred to have two statistical orientations with the oxygen atoms lying on the three planes parallel to the \bar{b} axis and the N atoms on the axis itself, 1.8 \AA from the Cl^- ion; the two orientations do not show the same frequency. The Cl^- atom and the two NO_3^- groups are so close to each other that the presence of the first excludes the other. This condition can be indicated by writing the content of Cl^- and NO_3^- in the channels along the \bar{b} axes as $\text{Cl}_x^- (\text{NO}_3)_{\bar{4}-2x}$ per unit cell, with x ranging from 0 to 2. The structural analysis does

not show any indication of the presence of SO_4^{2-} groups in the channels around the \bar{b} axes since no tetrahedral coordination is observed.

The least-squares refinement was performed leaving atomic coordinates, thermal parameters, and occupancies of disordered atoms to shift, with only the constraint of the symmetry of the space group $P6_3/mmc$ and of the ratio $\text{N}:\text{O} = 1:3$ in the nitrate group. On the basis of the results of the first cycles of refinement, two further conditions were assumed: on the \bar{b} axes, Cl and N contents obey the relationships $\text{Cl}^- = x$, $\text{NO}_3^- = 4-2x$ with $x = 0.7$; the two orientations of the NO_3^- groups (a and b , Table I) occur in the ratio $a : b = 2.6 : 1$.

TABLE I. Fractional atomic coordinates and isotropic thermal parameters with standard deviations in parentheses

Atom	Multiplicity	Occupancy factor	x/a	y/b	z/c	$B(\text{\AA}^2)$
Cu(1)	6	1	$\frac{1}{2}$	0	0	0.72(6)
Cu(2)	12	1	0.2012(1)	0	0	0.87(4)
Cu(3)	6	1	0.3352(3)	0.1676	$\frac{3}{4}$	0.82(7)
Cu(4)	12	1	0.3589(2)	0.0166(2)	$\frac{1}{4}$	0.97(5)
Cu(5)	2	0.30	0	0	0	2.36(71)
Cl(1)	6	1	0.2764(4)	0.1382	$\frac{1}{4}$	1.14(9)
OH(1)	24	1	0.4507(4)	0.3697(4)	0.0880(11)	0.88(12)
OH(2)	12	1	0.0743(4)	-0.0743	0.0961(15)	1.21(19)
OH(3)	24	1	0.6744(4)	0.7441(4)	0.1094(9)	1.15(12)
OH(4)	6	1	0.4454(6)	0.5546	$\frac{1}{4}$	1.88(32)
Cl(2)	2	0.35	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	3.69(71)
N	4	0.65	$\frac{3}{4}$	$\frac{1}{2}$	0.0557(58)	4.66(95)
O(a)	12	0.47	0.7123(10)	0.2877	0.0748(44)	2.73(58)
O(b)	12	0.18	0.6227(26)	0.3773	0.0335(88)	3.55(1.50)

During all the refinements reflections were given weights according to the following scheme: $\sqrt{w} = 1$ for reflections with $F_0 \leq 4F_{\min}$; $\sqrt{w} = 4F_{\min}/F_0$ for $F_0 > 4F_{\min}$; unobserved reflections were excluded from the calculations. Atomic scattering factor curves, corrected for anomalous dispersion, were taken from the *International Tables for X-ray Crystallography* (1962).

The final R value for the 328 observed reflections was 0.055. Refinements performed in the space groups $P\bar{6}2c$ and $P6_3mc$ do not exhibit significant atomic deviations from the higher symmetry. Therefore the space group better fitting the atomic arrangement was thought to be the centrosymmetrical one. The electrostatic balance was established assuming the possibility of a partial substitution of hydroxyl groups by water molecules; thus the chemical content in the unit-cell derived by the structural analysis is $\text{Cu}_{3.6}\text{Cl}_6[\text{Cl}_{0.7}(\text{NO}_3)_{2.6}](\text{OH})_{63.9} \cdot 2 \cdot \text{H}_2\text{O}$.

The specific density calculated with the preceding formula is 3.249 g cm^{-3} . Atomic coordinates and isotropic temperature factors are listed in table I. A table containing observed and calculated structure factors is deposited in the library of the Department of Mineralogy, British Museum (Natural History), whence copies may be purchased.

Discussion of the structure

The clinographic view of the structure of buttgenbachite is shown in fig. 1. The lists of bond lengths and bond angles with their standard deviations are included in Table II.

Cu(1), Cu(2), and Cu(4) ions have four oxygen atoms as nearest neighbours in an approximately square arrangement at an average distance of 1.967 Å (range: 1.949–1.983 Å), and two more atoms at distances in a range 2.732–2.968 Å. These

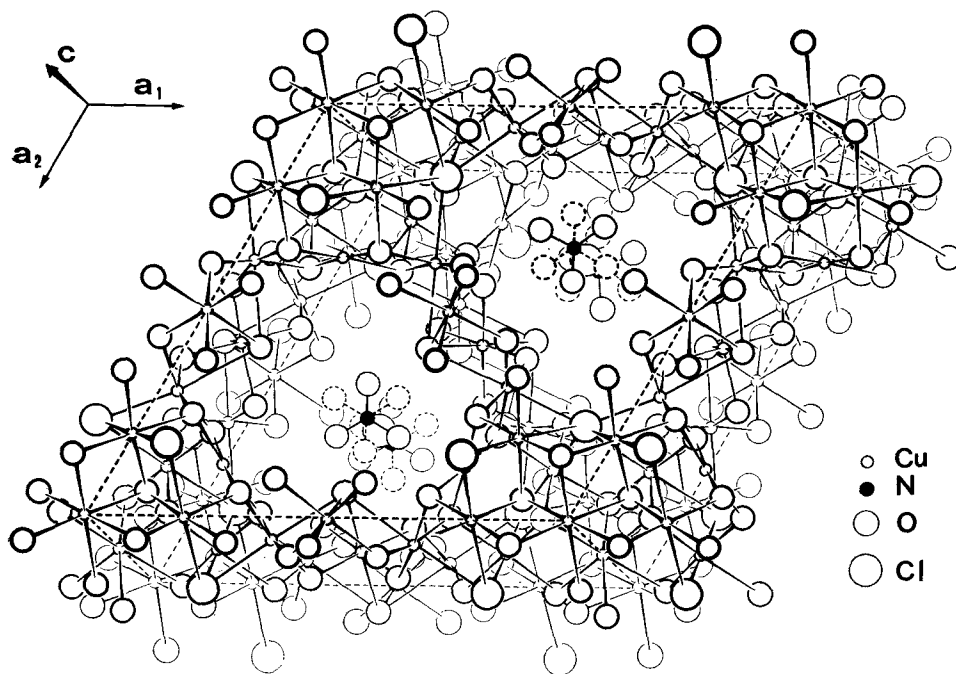


FIG. 1. Clinographic view of the buttgenbachite structure.

two atoms are 2 Cl for Cu(2), 1 Cl and 1 O atom for Cu(4) and 2 O atoms for Cu(1). The arrangement of ligands results in elongated tetragonal bipyramids. Cu(3) exhibits a square planar coordination with four Cu–O distances of 1.956 Å. Two more oxygens are 2.910 Å far from the central ion, on the same side of the square.

Cu(5) with occupancy about one-third the maximum for a site $\bar{3}m$, is 2.210 Å from six equivalent oxygen atoms. This kind of coordination is unusual for copper and energetically unfavoured; this fact may explain the partial occupancy of the site and the presence of a certain amount of Al, as revealed by spectrographic analysis.

The NO_3^- anions and a part of Cl^- ions are located in large channels around the $\bar{6}$ axes. They are not directly linked to the framework involving Cu coordination polyhedra. The two N–O distances have values of 1.26 and 1.24 Å.

The structure of buttgenschite is built up by a rigid three-dimensional skeleton formed by copper coordination polyhedra. These polyhedra share edges and corners to form a framework with large channels along \bar{b} axes. In each of these channels one Cl^- ion or two NO_3^- groups are located. The large Cl^- ions occupy positions corresponding to the widest openings in the channels.

TABLE II. *Interatomic distances and angles in buttgenschite*

(I) = $x, x-y, z$; (II) = $1-y, x-y, z$; (III) = x, y, z ; (IV) = $x-y, -y, -z$; (V) = $1-x, y-x, -z$; (VI) = $1-y, x-y, \frac{1}{2}z$; (VII) = $1-x, y-x, 1-z$; (VIII) = $1-x, 1-y, 1-z$; (IX) = $1-x, y-x, \frac{1}{2}+z$; (X) = $1-x, 1-y, \frac{1}{2}+z$; (XI) = $x, x-y, \frac{1}{2}z$

Bond lengths		OH(3)(V)-Cu(2)(I)-OH(3)(II)		88.8 ± 0.3°
Cu(1)(I)-OH(1)(I)	1.967 ± 0.006 Å × 4	-Cu(2)(I)-Cl(1)(III)	93.6	0.2
-OH(4)(I)	2.732 0.003 × 2	-Cu(2)(I)-Cl(1)(IV)	83.7	0.2
Cu(2)(I)-OH(2)(III)	1.949 0.008 × 2	Cl(1)(III)-Cu(2)(I)-Cl(1)(IV)	176.3	0.2
-OH(3)(V)	1.974 0.006 × 2	OH(3)(VII)-Cu(3)(I)-OH(3)(VIII)	97.1	0.3
-Cl(1)(III)	2.968 0.004 × 2	-Cu(3)(I)-OH(3)(IX)	82.4	0.3
Cu(3)(I)-OH(3)(VII)	1.956 0.007 × 4	-Cu(3)(I)-OH(3)(X)	172.3	0.3
Cu(4)(I)-OH(1)(I)	1.963 0.009 × 2	OH(1)(I)-Cu(4)(I)-OH(1)(XI)	98.2	0.3
-OH(3)(II)	1.983 0.007 × 2	-Cu(4)(I)-OH(3)(II)	90.1	0.3
-Cl(1)(III)	2.801 0.006	-Cu(4)(I)-OH(3)(VI)	169.6	0.3
-OH(4)(I)	2.912 0.006	-Cu(4)(I)-Cl(1)(III)	96.9	0.2
Cu(5)(I)-OH(2)(I)	2.210 0.007 × 6	-Cu(4)(I)-OH(4)(I)	83.0	0.2
N -O(a)	1.256 0.016	OH(3)(II)-Cu(4)(I)-OH(3)(VI)	81.0	0.3
N -O(b)	1.217 0.038	-Cu(4)(I)-Cl(1)(III)	88.2	0.2
		-Cu(4)(I)-OH(4)(I)	92.0	0.2
		Cl(1)(III)-Cu(4)(I)-OH(4)(I)	179.8	0.4
		OH(2)(I)-Cu(5)(I)-OH(2)(IV)	74.8	0.3
		O(a)(III)-N-O(a)(I)	118.1	1.5
		O(b)(III)-N-O(b)(I)	117.2	3.0
Bond angles				
OH(1)(I)-Cu(1)(I)-OH(1)(II)	91.9 ± 0.2°			
OH(4)(I)-Cu(1)(I)-OH(1)(I)	87.9 0.3			
OH(2)(III)-Cu(2)(I)-OH(2)(IV)	87.0 0.3			
-Cu(2)(I)-OH(3)(V)	92.2 0.3			
-Cu(2)(I)-OH(3)(II)	176.1 0.4			
-Cu(2)(I)-Cl(1)(III)	92.4 0.3			
-Cu(2)(I)-Cl(1)(IV)	90.3 0.3			

Relationships with connellite

The crystal structure of buttgenschite is closely related with that of connellite, which has a similar chemical formula and similar cell parameters. According to a recent structural determination (McLean and Anthony, 1972) the chemical formula of connellite is $\text{Cu}_{36.8}[(\text{SO}_4)_{1.6}(\text{NO}_3)_{0.4}]\text{Cl}_6(\text{OH})_{60}[(\text{OH})_2, (\text{Cl})_2, (\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ and the unit cell dimensions of the hexagonal cell are $a = 15.78$, $c = 9.10$ Å.

The space group assigned as the most probable to connellite was $P\bar{6}2c$. However, in our opinion the description of the crystal structure of connellite in this space group is not superior to the corresponding description in the centric space group ($P6_3/mmc$, as buttgenschite), not only because deviations from higher symmetry are very small but also because the partial disorder, located at the origin and in the channels around the \bar{b} axes, cannot be resolved by a lowering of symmetry to the space group $P\bar{6}2c$.

Notwithstanding the description in two different space groups, the copper-oxygen framework is very similar in connellite and buttgenschite. There are two main differences:

The partial substitution of O(7) by chlorine observed in connellite and not found in buttggenbachite. In the latter the electronic density at the position of OH(4), corresponding to O(7) site in connellite, rules out this possibility. However, the substitution chlorine–oxygen seems to be possible from a structural point of view: OH(4) is 2.732 and 2.912 Å from the copper ions to which it is coordinated and this could allow a complete mutual substitution. Secondly, buttggenbachite lacks the oxygen atom corresponding to O(12) of connellite. No residual positive electronic density was detected in the Fourier difference map. However, also in connellite the presence of O(12) is statistical and is not structurally required; this oxygen atom was assumed to belong to a water molecule with reduced occupancy. Its location in the channel at the boundary of the framework shows its probable zeolitic nature.

In both structures the trigonal antiprismatic coordination of the site at the origin, unusual for Cu atoms, explains why this site is only partially occupied. The occupancy of this site is about one-third the maximum in both buttggenbachite and connellite. The possibility that the two minerals form an isomorphous series can be easily explained taking into account that the framework is essentially the same and that compositional differences seem to occur mainly in the channels. However, a comparison of the results of the structural investigation on buttggenbachite with those for connellite shows that the isomorphous replacement is more complicated than was supposed earlier.

The atomic arrangements in the middle of the channels suggests ionic substitution of the kind $\text{SO}_4^{2-} \rightleftharpoons 2 \text{NO}_3^- \rightleftharpoons \text{Cl}^-$. In the present investigation, structural analysis reveals only the substitution $2 \text{NO}_3^- \rightleftharpoons \text{Cl}^-$; there was no evidence of oxygen atoms tetrahedrally arranged, excluding the possibility of a significant amount of SO_4^{2-} in our sample. Moreover, the occupancy at the middle of the channel is complete in buttggenbachite and expressible as $\text{Cl}_x(\text{NO}_3)_{2-2x}$ with $x \leq 1$.

On the other hand, a substitution $\text{SO}_4^{2-} \rightleftharpoons \text{NO}_3^-$, suggested as the more probable one by McLean and Anthony for connellite, seems less probable than the substitution $\text{SO}_4^{2-} \rightleftharpoons 2 \text{NO}_3^-$ with accomodation of two NO_3^- groups across the mirror normal to *c*.

Steric considerations can explain the preferential arrangement of the nitrate group in the (a) orientation of table I and the lack of water molecules in the channels when two nitrate groups are located in them. The structural elements in buttggenbachite and connellite easily explain the large range of substitutions in the channels. These substitutions seem to be of the same kind as those observed in zeolitic minerals. Assuming the occupancy of Cu at the origin to be one-third the maximum for that site as buttggenbachite and connellite structural analyses roughly confirm, a general chemical formula, describing the connellite–buttggenbachite series, can be: $\text{Cu}_{18}(\text{Cu}_{0.33}\square_{0.67})\text{Cl}_3[\text{Cl}_x, (\text{SO}_4)_y, (\text{NO}_3)_{2-2x-2y}](\text{OH})_{30}\{[\text{Cl}_z, (\text{OH})_{1-z}]_{1.66+x}, (\text{H}_2\text{O})_{3-1.66-x}\} \cdot n\text{H}_2\text{O}$ with $0 \leq n \leq 3$.

Acknowledgements. We thank Professor Cannillo of Pavia University for his computational assistance, and C.N.R. for its financial support.

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[*Manuscript received 29 December 1972*]