A single crystal X-ray study of a sulphate-bearing buttgenbachite, $Cu_{36}Cl_{7.8}(NO_3)_{1.3}(SO_4)_{0.35}(OH)_{62.2}.5.2H_2O$, and a re-examination of the crystal chemistry of the buttgenbachite – connellite series

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ABSTRACT

The single-crystal X-ray structure of a sulphate-bearing buttgenbachite, $Cu_{36}Cl_{7.8}(NO_3)_{1.3}$ $(SO_4)_{0.35}(OH)_{62.2}.5.2H_2O$, from Likasi, Democratic Republic of Congo, has been determined at 100 and 288 K. The basic framework of the structure is the same as has been previously reported for buttgenbachite, except for the identification of a hydrogen-bonded chloride ion (occupancy 0.6) at the origin instead of a Cu ion with partial occupancy. The nature of nitrate positional disorder along channels in the c direction and how this relates to the presence of other species such as chloride ions and water molecules and, most importantly, sulphate ions has been elucidated. One nitrate ion, with an occupancy of 0.18, lies at 2/3,1/3,1/4 and shares the site with a chloride ion (occupancy 0.30) and also a sulphate ion (occupancy 0.09); a second nitrate, with an occupancy of 0.24, lies at 2/3,1/3,0.084 and shares the site with a water molecule (occupancy 0.06). As a result, a formula of $Cu_{36}Cl_{7.8}(NO_3)_{1.3}$ $(SO_4)_{0.35}(OH)_{62.2}.5.2H_2O$ is obtained. Re-refinement of deposited data for a supposed connellite crystal from the Toughnut mine,Tombstone, Arizona gives a related, but different, pattern of anion substitution. No sulphate could be detected in the structure and it is evident that this structure refers to buttgenbachite. A nitrate nitrogen atom and a chloride ion are disordered at 2/3,1/3,1/4, the overall site being fully occupied. A chloride ion with ~0.5 occupancy is sited at the origin and the formula $Cu_{36}Cl_{7.9}(NO_3)_{1.1}(OH)_{63}.4H_2O$ is indicated. Re-refinement of a deposited data set for another buttgenbachite crystal from the Likasi mine reveals a partially occupied nitrate centred at 2/3,1/3, z and a partially occupied chloride at 2/3,1/3,1/4. Either $0.5Cl^-$, OH^-, H_2O or H_3O^+ is located at the origin. If the latter is the case, the stoichiometry for this buttgenbachite is $Cu_{36}Cl_{6.5}(NO_3)_{1.5}(OH)_{64}.5.5H_2O$. The present study has highlighted the fact that a range of compositions for buttgenbachite exists, depending on the pH and relative activities of chloride, nitrate and sulphate ions in solutions from which the mineral crystallizes.

KEYWORDS: buttgenbachite, connellite, solid solution, substitution, X-ray structure.

Introduction

THE complex basic hydrated copper(II) chloride-sulphate-nitrates connellite (sulphate end-member) and buttgenbachite (nitrate end-member) have been known for more than a century (connellite), although the common

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presence of nitrate in connellite was at first overlooked. End-member buttgenbachite was first described in 1925 (Ford and Bradley, 1915; Palache *et al.*, 1951). Stoichiometric complexity makes it difficult if not impossible to determine exact compositions by analysis. Ideal formulae of $Cu_{38}Cl_8(SO_4)_2(OH)_{64}.6H_2O$ and $Cu_{38}Cl_8(NO_3)_4$ $(OH)_{64}.4H_2O$ for connellite and buttgenbachite, respectively, have been suggested (Mandarino, 1999). Carbonate can substitute in part for sulphate or nitrate (Pollard *et al.*, 1989) and

both buttgenbachite and connellite are comparatively common in the oxidized portions of copper orebodies, even if generally present in small amounts (Pollard *et al.*, 1990; Williams, 1990).

A single-crystal X-ray structure of connellite (McLean and Anthony, 1972) revealed an intricate three-dimensional network of copper, chloride and hydroxide ions enclosing large channels parallel to *c*. In these channels, sulphate, nitrate, hydroxide and water molecules were considered to be disordered over several sites. The structure was refined in the acentric space group $P\bar{6}2c$, although it was noted that deviation from the alternative centrosymmetric space group $P6_3/mmc$ was very small. A formula for connellite derived from this structural analysis is $Cu_{36.8}Cl_8(SO_4)_{1.6}(NO_3)_{0.4}(OH)_{62}.8H_2O$. About the same time, Fanfani *et al.* (1973) reported the single-crystal X-ray structure of buttgenbachite, refined in space group $P6_3/mmc$. The same basic Cu(II) polyhedral framework as found by McLean and Anthony (1972) was present, although the disorder in the large channels was somewhat different; no evidence of any sulphate was found in the structure analysis, which yielded an overall formula $Cu_{36.6}Cl_{6.7}(NO_3)_{2.6}(OH)_{63.9}.4.2H_2O$.

Our interest in the series stems in part from the fact that connellite is readily synthesized in the laboratory (Pollard *et al.*, 1990), although buttgenbachite is not. In addition, connellite does occur in many deposits in small amounts, notably in Arizona (Anthony *et al.*, 1995) and in the Mt Isa Block, Australia (Sharpe, 1998). In further laboratory experiments, we failed to observe anion exchange between dissolved nitrate and solid connellite and thus our attention was drawn to the detailed nature of the apparent solid solution series. Furthermore, there are some puzzling aspects concerning the two structures as reported by McLean and Anthony (1972) and Fanfani *et al.* (1973). First, in both structures it has been reported that a copper ion with partial occupancy is located at the origin, bonded to six symmetry-equivalent hydroxide ions at 2.25(3) Å (connellite) or 2.210(7) Å (buttgenbachite) to form a peculiarly distorted octahedral coordination sphere (approximating a trigonal antiprism); this would represent a very unusual situation for copper(II). In fact, appropriate 'OH-Cu-OH' angles for this 'squashed' octahedral site are very close to being ideally tetrahedral (i.e. 106º) and thus it seemed more likely that the origin site is in fact occupied by a hydrogen-bonded chloride, hydroxide or hydronium ion, or

even by a water molecule. Secondly, attempts to refine the reported structures using deposited data failed to reproduce the reported results, either in space group $P\bar{6}2c$ (connellite) or $P6_3/mmc$ (buttgenbachite).

In order to clarify these issues, we have completely re-refined the structures of connellite and buttgenbachite using the deposited data sets to produce alternative but satisfactory new descriptions of their structures. It is now apparent that the supposed connellite of McLean and Anthony (1972) contains no sulphate and is in fact buttgenbachite. In addition, we have collected data sets at 100 K and 288 K for another crystal of Likasi buttgenbachite and have solved its structure, where in this case, although the tunnel sites contain predominantly nitrate and chloride, a small but significant amount of sulphate was also found.

For each of the structure determinations which are now described, a summary of the crystal data and structure refinement details is listed in Table 1, final atomic parameters are listed in Tables 2, 3, 4 and 5, and full lists of anisotropic thermal parameters (Table 9) and observed and calculated structure factors have been deposited with the Principal Editor and are available from the Mineralogical Society website at http://www.minersoc.org/pages/e_journals/dep_mat.htp

Likasi buttgenbachite structure determination using low-*T* (l00 K) data

A single crystal of buttgenbachite ~1.5 mm long, from the Likasi mine, Jadotville, Shaba Province, Democratic Republic of Congo, was purchased from the Mineralogical Research Company, San Jose, California, USA. From it was cut a fragment of dimensions $0.45 \times 0.25 \times 0.25$ mm and this was mounted on a Bruker SMART 1000 CCD-based diffractometer. Unit-cell dimensions were determined by least-squares refinement of the setting angles for 25 reflections within the range $3.0 < 2\theta < 50.6º$.

All data were collected at 100(2) K using graphite-monochromated Mo-*K*α radiation with omega scan increments of 0.3º. Data integration and reduction were undertaken using SAINT and XPREP (Bruker, 1995) and an empirical absorption correction determined using SADABS (Sheldrick, 1996) was applied. The structure was solved by direct methods (Sheldrick, 1990) and difference Fourier techniques and refined on F^2 by full-matrix least-squares methods (Sheldrick,

TABLE 1. Crystal data and structure refinement for: (a) Likasi Buttgenbachite (100 K data), (b) Liakasi Buttgrnbachite (288 K data), (c) Likasi Buttgenbachite (Fanfani *et al.* data), and (d) Toughnut mine 'Connellite' (McLean and Anthony data)

	(a)	(b)	(c)	(d)
Empirical formula	$H_{72.6}$ $Cl_{7.8}$ Cu_{36} $N_{1.3}$ $O_{72.7}S_{0.35}$	$H_{72.6}$ $Cl_{7.8}$ Cu_{36} $N_{1.3}$ $O_{72.7}S_{0.35}$	H_{75} $Cl_{6.5}$ Cu_{36} $N_{1.5}$ O_{74}	H_{71} $Cl_{7.9}$ Cu_{36} $N_{1.1}$ $O_{70.3}$
Formula weight	3829.76	3829.76	3798.48	3779.27
Temperature	100(2) K	288(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	1.5418 Å	1.5418 Å
Space group	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$
Unit-cell dimensions	$a = 15.739(2)$ Å	$a = 15.739(2)$ Å	$a = 15.750(3)$ Å	$a = 15.78$ Å
	$b = 15.739(2)$ Å	$b = 15.739(2)$ Å	$b = 15.750(3)$ Å	$b = 15.78$ Å
	$c = 9.127(1)$ Å	$c = 9.127(1)$ Å	$c = 9.161(2)$ Å	$c = 9.10$ Å
Volume	1958.0 Å³	1958.0 Å³	1968.0(7) Å³	1962.4 Å³
Z	1	1	1	1
Density (calculated)	3.248 Mg/m³	3.248 Mg/m³	3.205 Mg/m³	3.198 Mg/m³
Absorption coefficient	9.928 mm⁻¹	9.928 mm⁻¹	13.226 mm⁻¹	13.648 mm⁻¹
F(000)	1845	1845	1832	1819
Crystal size	0.45 × 0.25 × 0.25 mm	0.45 × 0.25 × 0.25 mm	0.01 × 0.03 × 0.27 mm	0.016 × 0.016 × 0.016 mm
θ range for data collection	1.49 to 27.95°.	1.49 to 25.26°.	6.49 to 80.66°.	6.48 to 73.60°.
Index ranges	$-19 \leqslant h \leqslant 19$, $-19 \leqslant k \leqslant 20$, $-11 \leqslant l \leqslant 11$	$0 \leqslant h \leqslant 16$, $-18 \leqslant k \leqslant 0$, $0 \leqslant l \leqslant 10$	$1 \leqslant h \leqslant 17$, $0 \leqslant k \leqslant 10$, $0 \leqslant l \leqslant 6$	$1 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 9$, $0 \leqslant l \leqslant 7$
Reflections collected	16406	1300	298	636
Independent reflections	898 [R(int) = 0.0314]	671 [R(int) = 0.1542]	298	634
Absorption correction	Empirical method (SADABS)	Empirical method (DIFABS)	None	Spherical method
Data / restraints / parameters	898 / 2 / 67	671 / 2 / 67	298 / 1 / 43	634 / 2 / 41
Goodness-of-fit on F^2	1.171	1.158	1.115	1.241
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0336$, $R_w = 0.1027$	$R_1 = 0.0542$, $R_w = 0.1837$	$R_1 = 0.0480$, $R_w = 0.1316$	$R_1 = 0.0852$, $R_w = 0.2392$
R indices (all data)	$R_1 = 0.0338$, $R_w = 0.1028$	$R_1 = 0.0613$, $R_w = 0.1892$	$R_1 = 0.0480$, $R_w = 0.1316$	$R_1 = 0.0858$, $R_2 = 0.2393$

1997) using all unique data corrected for Lorentz and polarization effects. Neutral atom scattering factors used were those given by Sheldrick (1997).

A starting set of coordinates, with occupancy factors dictated only by space group requirements, for the copper, chloride and hydroxide ions in the lattice (in agreement with the previously reported structures save for the supposed partially occupied Cu ion at the origin) was refined in space group $P6_3/mmc$ with anisotropic displacement parameters. Further refinement of the structure with a fully occupied chloride ion at the origin proceeded smoothly and sensibly. A difference-Fourier map then began to reveal the positions of atoms in the large channel parallel to *c*; a partially occupied site of a water molecule (OW) bonded to one of the Cu^{2+} ions (Cu3) was located in the $z = 3/4$ region, together with the nitrogen, N(1), and oxygen, O(1), atoms of a nitrate ion centred at $z = 1/4$ along the *c* axis. The oxygen atom O(1) was initially found at ~1.35 Å from the nitrogen atom N(1), and this seemed a little long for a N−O distance; however, refinement of this nitrate group with an N−O distance constrained to 1.20±0.01 Å (Sheldrick, 1997) proceeded smoothly. An inspection of the resulting temperature factors indicated

a higher than expected electron density at N(1) and a lower than expected electron density at O(1). Setting the population parameters of N(1) and O(1) to 35% and siting a chloride ion, Cl(4), with population parameter 30% at the N(1) position, allowed the N, O and Cl atoms to all refine with acceptable isotropic thermal parameters. A subsequent difference-Fourier map revealed a second, partially occupied nitrate, N(2),O(2), centred at 2/3,1/3, *z* and ~1.5 Å from nitrate N(1),O(1). This nitrate also had mixed occupancy but with a partially occupied water molecule, OW2, and refinement of this disordered site as above with population parameters of 24% for the nitrate atoms and 8% for the water molecule converged smoothly and gave acceptable thermal parameters for all atoms. Interestingly, no constraint on the N−O bond in this nitrate ion was required where a distance of ~1.20 Å resulted. At this stage the refinement appeared to be complete, with final R_1 and wR_2 values of 0.0421 and 0.131, respectively.

However, inspection of the final difference-Fourier map revealed a small peak ~0.5 Å from N(1) along the *c* axis and which was positioned approximately tetrahedrally at a distance of ~1.4 Å to each of the three oxygen atoms of

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) and site occupancy factors (sof) for Likasi Buttgenbachite (low-*T* data). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}	sof
Cu(1)	5000	0	0	10(1)	0.25
Cu(2)	2013(1)	0	0	11(1)	0.5
Cu(3)	3361(1)	1680(1)	7500	8(1)	0.25
Cu(4)	3590(1)	175(1)	2500	9(1)	0.5
Cl(3)	0	0	0	16(1)	0.050
Cl(1)	2772(2)	1386(1)	2500	14(1)	0.25
OH1	4505(2)	3699(2)	899(3)	11(1)	1.0
OH2	750(2)	−750(2)	985(6)	21(1)	0.5
OH3	6743(2)	7443(2)	1094(3)	10(1)	1.0
OH4	4444(3)	5556(3)	2500	29(2)	0.25
OW	5070(30)	2536(17)	7500	26(9)	0.0450
N(1)	6667	3333	2500	22(3)	0.0150
Cl(4)	6667	3333	2500	22(3)	0.0250
O(1a)	6222(4)	3778(4)	2500	17(4)	0.0450
O(1b)	6153(7)	3847(7)	2500	17(4)	0.0450
S(1)	6667	3333	3040(50)	20(6)	0.0150
O(1c)	6667	3333	320(50)	20(6)	0.0150
N(2)	6667	3333	860(20)	22(7)	0.0400
OW2	6667	3333	860(20)	22(7)	0.0100
O(2)	7113(8)	2887(8)	860(20)	22(4)	0.1200

the N(1),O(1) nitrate ion. As such it was assumed to be the sulphur atom, S(1), of a sulphate ion of quite low occupancy (~10%) with three of its oxygen atoms almost coincidental with the three oxygen atoms of the N(1),O(1) nitrate ion. That these two sets of oxygen atoms were not exactly coincidental was deduced from the initial position of oxygen O(1) which was originally found centred at ~1.35 Å from N(1) in the difference-Fourier map. This would have placed it ~1.5 Å from S(1) in a near perfect tetrahedral setting. However, when the N(1)−O(1) distance was constrained to be 1.20±0.01 Å this nitrate group also refined sensibly. Accordingly, O(1) was then split into O(1a), which was constrained to be 1.20±0.01 Å from N(1), and into O(1b), which was constrained to be 1.49±0.01 Å from S(1) and which gave close to a tetrahedral setting. The existence of this sulphate ion was confirmed with the subsequent location of the fourth oxygen atom, O(1c), ~1.5 Å from S(1) along the c axis, and during subsequent refinement this oxygen atom also was constrained to be 1.49±0.01 Å from S(1). The occupancy factor of the N(1),O(1a) nitrate ion was then reduced to ~20% to accommodate the presence of this sulphate ion. There was also evidence now that the chloride ion at the origin, Cl(3), was far from fully occupied and an occupancy of 60% was indicated. A final refinement was then performed via several strategic steps in which the occupancies of all the atoms constituting the large tunnel contents centred along (2/3, 1/3, z) and also the occupancy of the chloride ion Cl(3) at the origin were carefully adjusted to give a model which was both chemically and structurally sound, and which resulted in acceptable and similar isotropic thermal parameters for all the atoms concerned. Final R_1 and wR_2 values of 0.0336 and 0.103, respectively, were obtained for 888 data with $I > 2\sigma(I)$. Hydrogen atoms of the hydroxide ions or water molecules were not located in the structure and thus were not refined. However, for the requirement of charge balance, a small proportion of the assigned hydroxide ions must be protonated. The weighting scheme used was

$$w = 1/[\sigma^2(F_o)^2 + (0.0515P)^2 + 17.55P]$$

where $P = [\text{Max}(F_o)^2 + 2(F_c)^2]/3$ as defined by SHELX-97. Final atomic positions and equivalent isotropic thermal parameters are listed in Table 2 and the final contents of the large and small channels are shown in Table 7.

Likasi buttgenbachite structure determination using room-T (288 K) data

A second set of data was collected at 288 K using the same crystal as that used for the collection of the low-T data set. Cell parameters were taken to be equal to those of the low-T data set. All data were collected on an Enraf Nonius CAD4 diffractometer using graphite-monchromatized Mo-$K\alpha$ radiation. Data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using DIFABS (Walker and Stuart, 1983). The structure was solved by direct methods (Sheldrick, 1990) and difference-Fourier techniques and refined on F^2 by full-matrix least-squares methods (Sheldrick, 1997) using all unique data. The neutral atom scattering factors used were those given by Sheldrick (1997).

Although the positions of the atoms of the Cu(II) polyhedral framework were readily identified, it then proved difficult to decipher directly the exact nature of the nitrate occupancy in the large channels. Consequently, the atomic coordinates and site-occupancy parameters of the successful low-T structure solution were taken as a starting point for refinement using this room-temperature data set, which then allowed the nitrate occupancies to be resolved. Refinement converged smoothly to yield final values for R_1 and wR_2 of 0.054 and 0.184 for 578 data with $I > 2\sigma(I)$. The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.0900P)^2 + 17.00P]$ where $P = [\text{Max}(F_o)^2 + 2(F_c)^2]/3$ as defined by SHELX-97. Final atomic positions and equivalent isotropic thermal parameters are listed in Table 3.

There is no discernible difference between the two structures, save for the fact that the thermal parameters of the atoms comprising the nitrate and sulphate groups are somewhat larger at room temperature, as might be expected for the disordered portion of the structure.

Likasi buttgenbachite structure refinement using the data of Fanfani et al. (1973)

The structure was refined using the coordinates of Fanfani et al. (1973) for the copper, chloride and hydroxide ions constituting the Cu(II) polyhedral lattice, except for the reported partially occupied copper ion at the origin. At that stage, a difference-Fourier map revealed electron density at the origin equivalent to an oxygen atom (and subsequently considered to be an hydronium ion).

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) and site occupancy factors (sof) for Likasi Buttgenbachite (room-*T* data). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}	sof
Cu(1)	5000	0	0	13(1)	0.25
Cu(2)	2014(1)	0	0	13(1)	0.5
Cu(3)	3355(2)	1677(1)	7500	11(1)	0.25
Cu(4)	3592(1)	172(1)	2500	12(1)	0.5
Cl(3)	0	0	0	20(3)	0.0500
Cl(1)	2773(3)	1387(2)	2500	21(1)	0.25
OH1	4503(4)	3703(4)	918(6)	13(1)	1.0
OH2	749(4)	−749(4)	993(10)	24(2)	0.5
OH3	6744(4)	7452(4)	1101(5)	11(1)	1.0
OH4	4437(6)	5563(6)	2500	37(4)	0.25
OW	5080(70)	2540(30)	7500	30(20)	0.0450
N(1)	6667	3333	2500	28(6)	0.0150
Cl(4)	6667	3333	2500	28(6)	0.0250
O(1a)	6226(4)	3774(4)	2500	32(10)	0.0450
O(1b)	6155(4)	3845(4)	2500	32(10)	0.0450
S(1)	6667	3333	3045(50)	22(15)	0.0150
O(1c)	6667	3333	320(50)	22(15)	0.0150
N(2)	6667	3333	1000(40)	28(17)	0.0400
OW2	6667	3333	1000(40)	28(17)	0.0100
O(2)	7115(18)	2885(18)	1000(40)	29(9)	0.1200

This was refined isotropically and a further difference-Fourier map revealed the remaining contents of the channels. Firstly, there is a partially occupied water molecule in a site coordinated to one of the copper ions, Cu(3), not found by Fanfani *et al.* (1973) but common to the 'connellite' structure as reported by McLean & Anthony (1972) and to the structure of buttgenbachite reported here. Second, there is a nitrate group with nitrogen at 2/3,1/3, *z*, and another peak at 2/3,1/3,1/4 that has been attributed to a chloride ion in a site which is far from fully occupied. These two positions are too close (at 1.59 Å) to both be present simultaneously and the difference map revealed the fact that the nitrate group itself was only partially occupied. Occupancies for the two groups were chosen to give a unit-cell content of $1.5NO_3^-$ and $0.5Cl^-$. Refinement of the structure proceeded smoothly, giving acceptable thermal parameters for all atoms and confirmed the planarity of the nitrate group. Because of the limited number of data, only Cu ions were refined anisotropically. In the final refinement, the planarity of the nitrate group was fixed by linking the *z* coordinates of the N and O atoms and one reflection badly affected by extinction ($\bar{1}20$) was omitted from the calculations. In contrast with the report of Fanfani *et al.* (1973), no evidence was found for the existence of a second disordered oxygen position for the nitrate group centred at (2/3,1/3, *z*). No hydrogen positions could be reliably located in the structure. Final values of R_1 and wR_2 were 0.048 and 0.132, respectively, for all reported 298 observed data. It should be noted that the number of data deposited is 30 less than originally stated by Fanfani *et al.* (1973). The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.1P)^2 + 39.0P]$ where $P = [\text{Max}(F_o)^2 + 2(F_c)^2]/3$ as defined by SHELX-97. Final atomic positions and equivalent isotropic thermal parameters are listed in Table 4.

Toughnut mine 'connellite' structure refinement using the data of McLean and Anthony (1972)

The model proposed by McLean and Anthony (1972) could not be satisfactorily refined in either space group $P\bar{6}2c$ or $P6_3/mmc$, primarily due to the reported positions of the disordered sulphate and nitrate oxygen atoms. Thus a procedure similar to that described above was adopted, where the copper (excluding that at the origin), chloride and hydroxide ion positions were refined

TABLE 4. Atomic coordinates ($\times 10^4$), site occupancy factors (sof) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for Likasi Buttgenbachite (Fanfani *et al.* data). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}	sof
Cu(1)	5000	0	0	13(1)	0.25
Cu(2)	2012(2)	0	0	12(1)	0.5
Cu(3)	3354(3)	1677(2)	7500	11(1)	0.25
Cu(4)	3592(2)	168(2)	2500	15(1)	0.5
O(P)*	0	0	0	11(7)	0.0833
Cl(1)	2769(5)	1384(2)	2500	15(1)	0.25
OH1	4502(6)	3696(6)	889(13)	13(2)	1.0
OH2	749(5)	−749(5)	950(18)	18(3)	0.5
OH3	6736(7)	7436(6)	1082(13)	17(2)	1.0
OH4	4453(7)	5547(7)	2500	23(5)	0.25
OW	5020(80)	2510(40)	7500	30(20)	0.0625
Cl(4)	6667	3333	2500	26(12)	0.0208
N(2)	6667	3333	760(50)	40(20)	0.0625
O(2)	7103(7)	2897(7)	760(50)	24(9)	0.1875

* considered to be an H_3O^+ ion

isotropically in space group $P6_3/mmc$. Interestingly, at this point, R_1 was equal to 0.15 and, hence, significantly lower than that reported by McLean and Anthony for this stage of the refinement. A difference-Fourier map then revealed a peak at the origin, which subsequently refined satisfactorily as a chloride ion with 50% occupancy, but not as a fully occupied oxygen equivalent (as described above for the Likasi buttgenbachite structure using the data of Fanfani *et al.* (1973)). In addition, the map showed a peak at (1/3,2/3,1/4) and a further peak some 1.3 Å away from it at ($x,\bar{x}$,1/4), constituting a nitrate ion. The latter peak was of such a size as to indicate incomplete occupancy for the nitrate ion (~50%), while the former was much larger than expected for a N atom alone and suggested the significant co-occupation (~50%) of the site by a heavy ion such as chloride. Isotropic refinement of the model proceeded to give an N−O distance of 1.24 Å. The geometry of the nitrate group was then fixed so that the N−O distance was 1.20±0.01 Å. Finally, a peak corresponding to a partially occupied water molecule site bonded to one of the Cu ions was again revealed. It may be noted that evidence for the presence of a sulphate ion in the channel was not readily apparent. Thus, this sample from the Toughnut mine, Arizona, is in fact a buttgenbachite. We note that the crystal sample used by McLean and Anthony (1972) was not analysed and the presence of sulphate in it was

merely assumed. Refinement of the structure, with anisotropic thermal parameters for the Cu atoms only, in view of the quality of the data available, proceeded smoothly. Sensible thermal parameters were obtained for all atoms; occupancy factors of 0.45:0.55 for the disordered chloride:nitrate site and 1/6th occupancy for the water molecule bonded to copper in the channels gave a perfectly acceptable structure. Final values of R_1 and wR_2 were 0.085 and 0.239, respectively, for all 633 reported data. It should be noted that the number of data refined by McLean and Anthony (1972) was reported as 493, this number corresponding to those reflections that were considered to be observed. However, there was no indication of which reflections had been omitted from the refinement in the deposited data. The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.1P)^2 + 100P]$ where $P = [\text{Max}(F_o)^2 + 2(F_c)^2]/3$ as defined by SHELX-97. Final atomic positions and equivalent isotropic thermal parameters are listed in Table 5.

Description of the Likasi Buttgenbachite structure

The structure of Likasi buttgenbachite, determined in the present work, is essentially the same as that previously described by Fanfani *et al.* (1973) for a buttgenbachite specimen from this type locality, and also that described by McLean and Anthony

TABLE 5. Atomic coordinates ($\times 10^4$), site occupancy factors (sof) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for Toughnut mine 'Connellite' (McLean and Anthony data). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}	sof
Cu(1)	5000	0	0	15(1)	0.25
Cu(2)	2024(2)	0	0	14(1)	0.5
Cu(3)	3346(3)	1673(1)	7500	13(1)	0.25
Cu(4)	3590(2)	162(2)	2500	13(1)	0.5
Cl(3)	0	0	0	15(4)	0.0417
Cl(1)	2769(4)	1385(2)	2500	21(1)	0.25
OH1	4509(6)	3698(6)	901(11)	15(2)	1.0
OH2	765(5)	−765(5)	959(19)	30(3)	0.5
OH3	6740(6)	7443(6)	1082(11)	15(2)	1.0
OH4	4439(7)	5561(7)	2500	20(4)	0.25
OW	5020(100)	2510(50)	7500	40(30)	0.0417
Cl(4)	6667	3333	2500	23(4)	0.0375
N(1)	6667	3333	2500	23(4)	0.0458
O(1)	6213(5)	3787(5)	2500	22(7)	0.1375

(1972) for a supposed connellite specimen from the Toughnut mine, Tombstone, Arizona, but with some important, yet subtle, differences. The structure consists of the same elegant, three-dimensional lattice formed by the corner- and edge-sharing of Cu(II) polyhedra via common O or Cl atoms, and is shown in Fig. 1. A dominant feature of the resulting polyhedral framework structure is a large channel parallel to *c* and centred around the $\bar{6}$ axis along (2/3,1/3,*z*) wherein NO_3^-, Cl^- and SO_4^{2-} ions and H_2O molecules may reside in a disordered manner with variable occupancies. A further feature is the narrow channel in the framework also parallel to *c* but centred around (0,0,*z*). In this channel, oxygen atoms around the origin result in an interesting 'squashed' octahedral array. This site apparently may host different ionic species with varying occupancies; in the present structure this site is considered to be 60% occupied by Cl^- ions. Details of the occupancies of the various sites in the large and small channels are given in Table 7.

In previous descriptions of the buttgenbachite type structure by Fanfani *et al*. (1973) and McLean and Anthony (1972) the Cu^{2+} ions were, with one exception, considered to be 6-fold coordinated by OH^- and Cl^- ions and H_2O molecules, where this 6-fold coordination was of a '4 + 2' elongate tetragonal bipyramidal configuration (i.e. tetragonally elongate octahedral). Such an octahedral elongation is characteristic of Cu(II) due to the Jahn-Teller effect, and is

enhanced in buttgenbachite when the large Cl^- ion forms part of the coordination polyhedron. However, in order to sustain this structural description, several rather distant O atoms (with very long Cu−O distances of ~2.9 Å) must be considered to be part of the coordination sphere for two of the four independent Cu^{2+} ions, and for one of them even results in a quite unusual 7-fold coordination. In view of the questionable validity of this standpoint, in the present structure determination for Likasi buttgenbachite the stereochemistry of the Cu^{2+} ions in the polyhedral framework has been carefully reinterpreted.

Bond lengths and selected angles for the Cu(II) polyhedra are summarized in Table 6. This shows that the four independent Cu(II) polyhedra contain only slightly distorted square planar arrangements of oxygen atoms (OH^- ions) about the Cu^{2+} ion, where these four nearest-neighbour oxygen atoms lie in the fairly close range of 1.951−1.987 Å (at an average value of 1.962 Å for the 16 distances). For Cu1 and Cu2 there are two more atoms at somewhat greater distances which complete tetragonal bipyramidal poly-hedra; for Cu1 they are both O atoms (OH^- ions) at 2.739 Å, and for Cu2 they are both Cl^- ions at 2.964 Å. For Cu3 and Cu4 there is only one further atom which may be considered to be coordinated and in each case it completes a square pyramidal polyhedron; for Cu3 this is an O atom (H_2O molecule) at 2.35 Å and for Cu4 it is a Cl^- ion at 2.783 Å. The Cu−O distances for the more
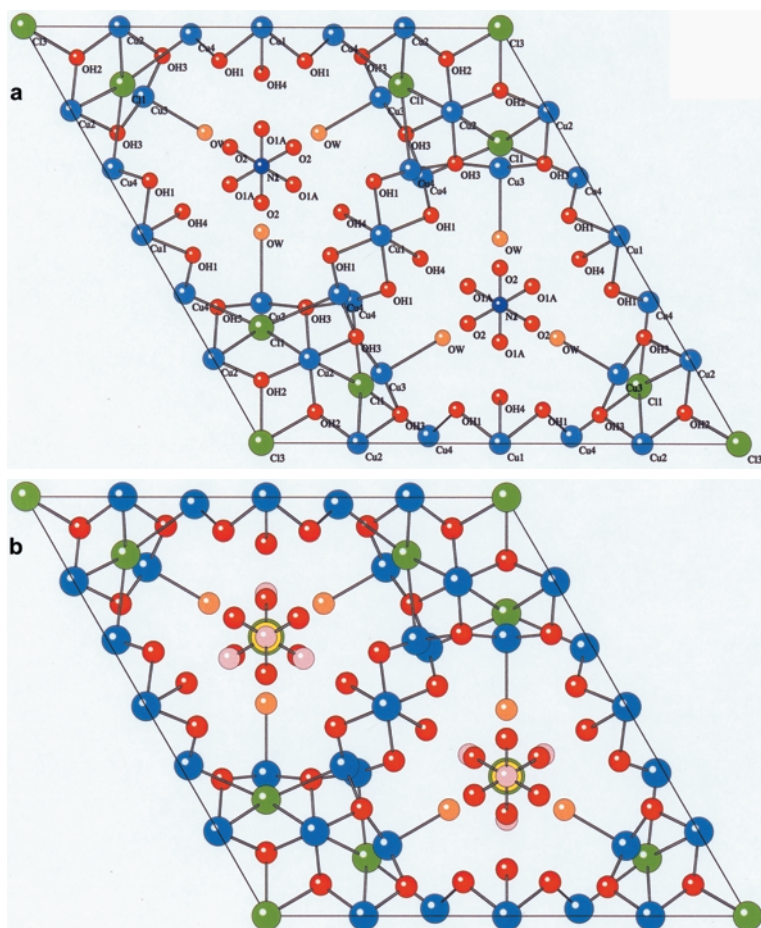
FIG. 1(*a*) View down *c* of a single unit cell of Likasi buttgenbachite showing details of the structure. Note that the chloride ion Cl(4), the sulphate ion S(1),O(1b),O(1c) and the water molecule OW2, which are disordered with the two nitrate ions N(1),O(1a) and N(2),O(2) in the 'large' channel sites, have been omitted for clarity. The oxygen atom of the lattice water molecule OW (pale orange) has been coloured differently from all other oxygen atoms in the structure (red) in order to emphasize the strategic tunnel site location. (b) View down *c* of a single unit cell of Likasi buttgenbachite showing details of the disordered nature of the structure in the 'large' channel sites. Of the atoms which lie on the $\bar{6}$ axis, only S(1) (yellow), Cl(4) (green) and O(1c) (pink) have been shown; the remaining atoms N(1), N(2) and OW2 are effectively obscured. For the associated off-axis atoms, the nitrate ion oxygen atoms, O(1a) and O(2), are shown in red while the sulphate ion oxygen atom O(1b) is shown in pink which allows it to be differentiated from the immediately adjacent nitrate oxygen atom O(1a).

distant O atoms previously considered to form part of the coordination spheres of Cu3 and Cu4 are included for interest in Table 6. Accordingly, the stereochemistry of Cu(II) in buttgenbachite is most simply described as tetragonal bipyramidal 6-coordinate for half the Cu^{2+} ions and square pyramidal 5-coordinate for the other half.

A resulting structural feature is the narrow channel which exists in this Cu(II) polyhedral framework and which, like the large channel, runs parallel to the *c* axis but is centred around $(0,0,z)$. As mentioned previously, this produces a peculiar distorted octahedral polyhedron of six OH^{-} ions around the origin, where the distortion involves significant flattening along one of the $\bar{3}$ axes of the octahedron. This gives an atomic array of trigonal point symmetry, with six equally disposed O atoms around the origin (see Fig. 1), and is

TABLE 6. Selected bond lengths (Å) and angles (º) for Likasi buttgenbachite (100 K data) with estimated standard deviations in parentheses.

Bond lengths (Å)			Selected angles (º)	
Cu1	−OH1	1.969(3) ×4	OH1−Cu1−OH1	91.8(2), 88.3(2), 180.0
	−OH4	2.739(4) ×2	OH1−Cu1−OH4	87.8(1), 92.2(1)
			OH4−Cu1−OH4	180.0
Cu2	− OH2	1.951(3) ×2	OH2−Cu2−OH2	88.5(3)
	−OH3	1.972(3) ×2	OH3−Cu2−OH3	88.9(2)
	−Cl(1)	2.964(1) ×2	OH2−Cu2−OH3	91.4(2), 176.6(2)
			OH2−Cu2−Cl(1)	92.7(1), 90.3(1)
			OH3−Cu2−Cl(1)	93.2(1), 83.9(1)
			Cl(1)−Cu2−Cl(1)	176.0(1)
Cu3	−OH3	1.950(3) ×4	OH3−Cu3−OH3	82.4(2), 97.0(2), 171.7(2)
	−OW	2.33(5)	OH3−Cu3−OW	94.2(1)
	{−OH2	2.889(6) ×2 }*		
Cu4	−OH1	1.940(3) ×2	OH1−Cu4−OH1	97.7(2)
	−OH3	1.987(3) ×2	OH3−Cu4−OH3	80.5(2)
	−Cl(1)	2.783(1)	OH1−Cu4−OH3	90.5(1), 169.1(1)
	{−OH4	2.937(5) }*	OH1−Cu4−Cl(1)	97.4(1)
			OH3−Cu4−Cl(1)	88.6(1)
Cl(3)−OH2		2.233(6) ×6	OH2−Cl(3)−OH2	104.9(1), 75.1(1), 180.0
N(1) −O(1a)		1.21(1)	O(1)−N(1)−O(1)	120.0
N(2) −O(2)		1.22(2)	O(2)−N(2)−O(2)	120.0

*Not considered bonded, but included for comparison with previously reported structures.

perhaps best described as approximating a trigonal antiprism. In the present structure this site is considered to be 60% occupied by a Cl⁻ ion, Cl(3), which is 2.233 Å from each of the six equivalent hydroxyl groups (OH2). Appropriate OH-Cl-OH angles are close to ideal tetrahedral values (see Table 6) and suggest that hydrogen bonding is an important control on the content of this lattice site. In previous structure descriptions, Fanfani *et al*. (1973) and McLean and Anthony (1972) have proposed the presence of Cu^{2+} ions in this site. Partial occupancy was cited as a possible reason for the unusual 6-coordinate geometry about Cu(II) despite the energetically unfavourable nature of this arrangement. Indeed, almost without exception, the d^9 configuration makes Cu(II) subject to classic tetragonal Jahn-Teller distortion if placed in an octahedral coordination environment, and hence it seems improbable that Cu^{2+} ions would seek to occupy this position in the buttgenbachite lattice.

The nitrate ions are located in two crystallographically independent sites in the large 'open' channels of the structure centred on the $\bar{6}$ axis and in each case are not directly linked to the surrounding framework of the Cu(II) coordination polyhedra, although some hydrogen bonding is evident. One nitrate (N1, O1a) is centred at (2/3,1/3,1/4), in the same position as found in this study using the data of McLean and Anthony (1972) for the supposed connellite structure, and occupies the site to an 18% level. The other nitrate (N2, O2) is centred at (2/3,1/3,z) and also symmetrically at (2/3,1/3,½−z) across the mirror plane normal to *c*. This places it ~1.5 Å on each side of the first nitrate, which is located on the mirror, and in a similar position to that found in this study using the data of Fanfani *et al*. (1973) for their sample of Likasi buttgenbachite (see Table 7). Although it only occupies the site to a 24% level, this nitrate ion is structurally complementary to the 18% occupancy of the other nitrate in the adjacent mirror plane site and to the 9% occupancy of the associated sulphate ion located either side of this mirror plane, although all these sites are never occupied simultaneously. It may be

TABLE 7. Comparison of the contents of the large and small channels in the various buttgenbachite crystals studied, with the % occupancy of the site shown in parentheses.

Site	Fanfani *et al*. data	McLean and Anthony data	Present data*
Large channels centred along (2/3,1/3,z)			
Site #1	Cl^-	Cl^-	NO_3^-
at z = 1/4	(25%)	(45%)	(18%)
		NO_3^-	Cl^-
		(55%0	(30%)
at z ~0.20 (and ~0.30)			SO_4^{2-}
			(9%)
Site #2	NO_3^-		NO_3^-
at z ~ 0.08 (and ~ 0.42)	(37.5%)		(24%)
			H_2O
			(6%)
Lattice H_2O (OW)	(25%)	(17%)	(18%)
at (~0.50, ~0.25, 3/4)			
Small channels centred along (0,0,z)			
Origin	H_3O^+	Cl^-	Cl^-
at z = 0,1/2	(100%)	(50%)	(60%)

* intepreted as a buttgenbachite with a small amount of SO_4^{2-} associated with site #1

noted that the presence of chloride (30% occupancy) and water (6% occupancy) brings the overall occupancy of this collection of adjacent sites in the large tunnels to a total of 87% which is crystallographically sound. Further, the perfectly staggered orientation of the two nitrate ions (at z = 1/4 and $z \approx$ 0.08) and the associated sulphate ion along the $\bar{6}$ axis is apparently controlled by hydrogen bonding to one of the hydroxyl ions (OH1) in the Cu(II) polyhedral framework, where in the present structure O–O distances of 2.86(1) Å, 3.021(8) Å and 2.88(1) Å from OH1 to O2, O1a and O1b respectively have been found. It may also be noted that O2 is only 3.21(2) Å away from the coordinated water molecule OW and hence the possibility of further hydrogen bonding exists in this case.

It is important to note that the large channel becomes significantly constricted once per c periodicity and at its narrowest point the distance from the axis of the channel to the framework is only 2.2 Å, i.e. to the OW site (the water molecules bonded to Cu3). At its widest it is 3.8 Å, i.e. to the OH1 site (the OH$^-$ ions bonded to Cu1 and Cu4), as shown in Fig. 1. It should also be noted that the water molecules at the OW site are not only bonded to Cu3 but are also

hydrogen bonded to adjacent hydroxyl groups OH3 and OH4 with O–O separations of 3.14(4) and 2.70(1) Å, respectively. It is therefore not unexpected that the 'double nitrate/sulphate group moiety' occupies the widest part of the large channel in Likasi buttgenbachite, and it may be further deduced that the coordinated water molecules (OW) are an essential part of the structure, appearing to act as a control over the 'contents' and their location in the large channels in any buttgenbachite sample. Finally, it may be concluded that the location of the sulphate ion in this buttgenbachite, i.e. in a 4f site along 2/3,1/3,z with the sulphur atom centred at z ~0.30 and ~0.20, and hence on each side of the mirror plane at z = ¼, is probably the preferred location for sulphate ions in any buttgenbachite or connellite species.

Potential end-member compositions of the buttgenbachite–connellite series

On the basis of the structural results reported above, it is possible to suggest possible end-member compositions for buttgenbachite. Because of the nature of the disorder over several sites including the channels in the structure and at the origin, as summarized in

TABLE 8(*a*). Anisotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for Likasi buttgenbachite (100 K data).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	8(1)	11(1)	12(1)	−2(1)	−1(1)	5(1)
Cu(2)	11(1)	9(1)	11(1)	2(1)	1(1)	4(1)
Cu(3)	11(1)	7(1)	8(1)	0	0	6(1)
Cu(4)	7(1)	9(1)	8(1)	0	0	2(1)
Cl(3)	14(2)	14(2)	20(3)	0	0	7(1)
Cl(1)	15(1)	11(1)	16(1)	0	0	8(1)
OH1	10(1)	10(1)	11(1)	1(1)	1(1)	5(1)
OH2	14(2)	14(2)	23(2)	−5(1)	5(1)	−1(2)
OH3	12(1)	10(1)	10(1)	1(1)	1(1)	6(1)
OH4	46(4)	46(4)	15(3)	0	0	40(4)

Table 8(*b*). Anisotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for Likasi buttgenbachite (288 K data).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	9(1)	13(1)	17(1)	−3(1)	−1(1)	7(1)
Cu(2)	12(1)	12(1)	16(1)	3(1)	1(1)	6(1)
Cu(3)	14(1)	9(1)	11(1)	0	0	7(1)
Cu(4)	9(1)	12(1)	12(1)	0	0	2(1)
Cl(3)	24(5)	24(5)	14(6)	0	0	12(2)
Cl(1)	21(2)	14(2)	30(2)	0	0	10(1)
OH1	8(3)	14(3)	15(3)	4(2)	3(2)	4(3)
OH2	21(4)	21(4)	24(5)	−4(2)	4(2)	4(4)
OH3	14(3)	11(3)	11(3)	3(2)	2(2)	9(3)
OH4	58(9)	58(9)	17(7)	0	0	45(10)

Table 8(*c*). Anisotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for Likasi buttgenbachite (Fanfani *et al*. data).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	9(1)	11(2)	20(4)	0(2)	0(1)	5(1)
Cu(2)	14(1)	13(1)	9(3)	3(1)	2(1)	7(1)
Cu(3)	15(2)	13(1)	7(4)	0	0	7(1)
Cu(4)	13(1)	14(1)	17(3)	0	0	5(1)

Table 8(*d*). Anisotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for Toughnut mine 'connellite' (McLean and Anthony data).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	10(1)	19(2)	19(3)	−5(2)	−2(1)	10(1)
Cu(2)	13(1)	14(1)	16(2)	4(1)	2(1)	7(1)
Cu(3)	22(2)	12(1)	9(3)	0	0	11(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$

Table 7, it is difficult to choose 'ideal' compositions with certainty. Given the basic common structural motif, and the siting of NO_3^- ions in the channels, stoichiometries can be derived if the origin site has a pre-determined site occupancy. It should be noted that in the newly determined structure of buttgenbachite, nitrates are found at both sites occupied separately in the structures derived using the McLean and Anthony (1972) and Fanfani *et al*. (1973) data (see Table 7). Thus end-member compositions can be envisaged by taking one or other, or both, of the nitrate group sites as being fully occupied.

The basic structural motif formed by Cu1, Cu2, Cu3, Cu4, Cl(1), OH1, OH2, OH3 and OH4 has a neutral charge distribution. Full occupancy of a nitrate ion at 2/3,1/3,1/4, as in the structure corresponding to the McLean and Anthony (1972) data, gives a charge-neutral formula of $Cu_{36}Cl_6(NO_3)_2(OH)_{64}.10H_2O$ if the origin and OW sites are fully occupied by water molecules (note, however, that in none of the structures is the OW site anywhere nearly fully occupied and much of the channel water appears to be zeolitic in nature). If H_3O^+ is at the origin, two of the OW water molecules would have to be deprotonated to give the same overall formula. Alternatively, if the origin is fully occupied by a Cl^- ion, 2 protons will need to be distributed over the hydroxide sites, yielding a formula of $Cu_{36}Cl_8(NO_3)_2(OH)_{62}.10H_2O$.

In a structure akin to that derived using the data of Fanfani *et al*. (1973), the nitrate group has N at the 4*f* site (1/3,2/3,*z*). Appropriate protonation of lattice hydroxide ions to maintain charge neutrality results in a stoichiometry of $Cu_{36}Cl_6(NO_3)_4(OH)_{62}.12H_2O$ if both the origin and OW sites are fully occupied by water molecules. With H_3O^+ at the origin, the formula remains constant but with a fully occupied origin chloride ion becomes $Cu_{36}Cl_8(NO_3)_4(OH)_{60}.12H_2O$. In the structure determined here for the data of Fanfani *et al*. (1973), the nitrate is associated with a chloride ion at the 2*d* site (2/3,1/3,1/4), both having reduced occupancy and both being too close to each other to be present simultaneously.

There seems little point in working through other possibilities involving variation of the substituent at the origin. It is sufficient to draw attention to the fact that there are two sites for substitution of nitrate, both of which may accommodate chloride or water if partially occupied, and only one site for substitution of sulphate, in the large channels. Further, the origin site in the small channels can accommodate varying amounts of water molecules, chloride or hydronium ions. Thus there exists a family of potential end-members with individual examples adopting a number of substitutional patterns. It seems probable that although the coordinated water molecules, OW, in the large channels may not be found to be fully occupied in any example (see Table 7), their existence in these large channels seems structurally significant as they define the 'constriction' point in the channel, and indeed their level of occupancy may be important in determining the overall large channel composition. Accordingly, the composition of any single buttgenbachite crystal, which may indeed be zoned, will reflect the relative activities of chloride and nitrate ions, and the particular pH, in the solution from which it crystallizes.

Finally, we note that nitrate and/or sulphate, and perhaps carbonate (Pollard, *et al*., 1989), are essential to the buttgenbachite–connellite series. This must be due to some kind of template effect concerning the stabilization of the channels in the structure. Without small amounts of sulphate and nitrate, the basic double-salt phases that form in the system at room temperature are claringbullite ($Cu_4Cl(OH)_7$) and polymorphs of composition $Cu_2Cl(OH)_3$ (botallackite, atacamite, paratacamite, clinoatacamite).

Acknowledgements

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