The Canadian Mineralogist
Vol. 33, pp. 633-639 (1995)

CLARINGBULLITE: A Cu^{2+} OXYSALT WITH Cu^{2+} IN TRIGONAL-PRISMATIC COORDINATION

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ABSTRACT

The crystal structure of claringbullite, $Cu_4Cl[Cl_{0.29}(OH)_{0.71}](OH)_6$, hexagonal, a 6.6733(5), c 9.185(1) Å, V 354.22(6) Å^3, $Z = 2$, space group $P6_3/mmc$, has been solved by trial-and-error methods and refined by least-squares methods to an R index of 3.4%, a wR index of 3.2%, and an S factor of 1.35 using 227 unique observed [$I \geq 2.5\sigma(I)$] reflections. The chemical formula of claringbullite has been revised as a result of this determination of the crystal structure. Claringbullite contains two Cu positions. The Cu(1) position is octahedrally coordinated by four (OH) groups and two Cl atoms. The Cl(1) atoms are located in the apical positions of a (4 + 2)-distorted octahedron, the distortion of which is attributed to the Jahn–Teller effect. The Cu(2) position is coordinated by six (OH) groups in a distorted trigonal prismatic arrangement. The $Cu(1)\phi_6$ octahedra share edges to form sheets of octahedra parallel to (001), with every fourth octahedral site vacant. These sheets of octahedra share Cl atoms along [001], and thus claringbullite has a framework structure. The stacking of sheets of octahedra is such that the holes in the sheets are collinear, forming channels through the structure parallel to [001]. The Cl(2) position, which is partially occupied by (OH), is located in these channels, at a point midway between the sheets of octahedra. The Cu(2) position is located between the sheets, further linking the $[Cu(1)_3\square]\phi_8$ sheets of octahedra into a framework.

Keywords: claringbullite, copper oxysalt, crystal structure, Bisbee, Arizona.

SOMMAIRE

Nous avons affiné la structure cristalline de la claringbullite, $Cu_4Cl[Cl_{0.29}(OH)_{0.71}](OH)_6$, hexagonale, a 6.6733(5), c 9.185(1) Å, V 354.22(6) Å^3, $Z = 2$, group spatial $P6_3/mmc$, par méthodes d'essais par tâtonnements et par moindres carrés jusqu'à un résidu R de 3.4% ($wR = 3.2\%$, facteur S égal à 1.35) en utilisant 227 réflexions uniques observées [$I \geq 2.5\sigma(I)$]. Nous avons corrigé la formule chimique de cette espèce à la lumière de nos résultats. La claringbullite contient deux positions à Cu. Le Cu(1), à coordinence octaédrique, est entouré de quatre groupes (OH) et deux atomes de Cl. Les atomes Cl(1) occupent les positions apicales d'un octaèdre difforme, dont l'agencement (4 + 2) résulte de l'effet de Jahn–Teller. Le Cu(2) est coordonné à six groupes (OH) dans un agencement trigonal prismatique difforme. Les octaèdres $Cu(1)\phi_6$ partagent des arêtes pour former des feuillets d'octaèdres parallèles à (001), chaque quatrième site octaédrique étant vacant. Ces feuillets d'octaèdres partagent des atomes de Cl le long de [001], ce qui attribue à la claringbullite une charpente tridimensionnelle. L'empilement des feuillets d'octaèdres produit des trous colinéaires dans les feuillets, ces canaux au travers de la charpente étant parallèles à [001]. L'atome Cl(2), qui semble en partie remplacé par le (OH), est situé dans ces canaux, à distance égale entre deux feuillets adjacents. La position du Cu(2), entre les feuillets octaédriques, contribue au rattachement des feuillets d'octaèdres $[Cu(1)_3\square]\phi_8$ dans la charpente.

Mots-clés: claringbullite, oxysel de cuivre, structure cristalline, Bisbee, Arizona.

INTRODUCTION

Claringbullite was described by Fejer *et al.* (1977), who reported the formula to be $Cu_4Cl(OH)_7{\cdot}nH_2O$ ($n \approx ½$); it occurs at Bisbee, Arizona, at the M'sesa mine, Kambowe, Katanga, Zaire and the Nchanga open pit, Zambia. As part of our general interest in Cu^{2+} oxysalt minerals (Burns 1994, Burns *et al.* 1995, Eby & Hawthorne 1993), we have determined the structure of claringbullite and report the results here.

EXPERIMENTAL

The claringbullite crystals used in this study are from Bisbee, Cochise County, Arizona, and were graciously provided for study by Mr. Forrest Cureton. A thin plate of claringbullite was mounted on a Nicolet $R3m$ automated four-circle diffractometer. Forty reflections over the range $15° < 2\theta < 45°$ were centered using graphite-monochromated Mo$K\alpha$ X-radiation. The unit-cell dimensions (Table 1) were derived from the setting angles of the forty automatically aligned reflections by least-squares techniques. Data were collected using the θ–2θ scan method, with a scan

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TABLE 1. MISCELLANEOUS INFORMATION FOR CLARINGBULLITE

Space Group	$P6_3/mmc$	Crystal Size (mm)	0.36x0.59 x0.02
a (Å)	6.6733(5)		
c (Å)	9.185(1)	Total Ref.*	1346
V (Å^3)	354.22(6)	I ≥ 2.5σ(I)	227
		R_{INT}	1.9%
μ	12.37 mm^{-1}	Final R	3.4%
D_{CALC}	3.882 g/cm^3	Final wR	3.2%
F(000)	396.7	Final S	1.35

Largest difference peak in Fourier map 0.76 e/Å^3

Largest difference hole in Fourier map -1.18 e/Å^3

Unit-cell contents $2\{Cu_4Cl[Cl_{0.29}(OH)_{0.71}](OH)_6\}$

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1/\sigma^2(F)$

$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, for m observations and n parameters

* Total Ref. is the total number of reflections collected minus the number of reflections omitted due to absorption correction.

range of 2.3°. A variable scan-rate inversely proportioned to the peak intensity was used, with maximum and minimum scan-rates of 29.3°2θ/min and 3.9°2θ/min, respectively. A total of 1535 reflections was measured over the range $4° \leq 2\theta \leq 60°$, with index ranges $0 \leq h \leq 9, -9 \leq k \leq 0, -12 \leq l \leq 12$. Two standard reflections were measured every fifty-eight reflections; there were no significant changes in their intensities during data collection. An empirical absorption correction, based on 36 psi-scans of each of 11 reflections over the range $7 \leq 2\theta \leq 59°$ was applied, with the assumption that the crystal can be modeled as a {001} plate. The absorption correction reduced R(azimuthal) from 8.3 to 2.6%. One hundred and eighty-eight reflections with a plate-glancing angle less than 5° were discarded. The value of 5° was determined by using a range of glancing angles between 3 and 20°, and determining where the effect of increasing the glancing angle produced no improvement in the refinement. The remaining data were corrected for Lorentz, polarization and background effects, and equivalent reflections were merged, giving an R_{INT} of 1.9%; of the 1347 reflections remaining after the absorption correction, there were 227 unique observed reflections [$I \geq 2.5\sigma$ (I)].

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. R indices are of the form given in Table 1 and are expressed as percentages. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout this study.

Systematic absences indicate that the probable space-groups of claringbullite are $P6_3/mmc$, $P\bar{6}2c$, and $P6_3mc$; intensity statistics favor the presence of a center of symmetry. Attempts to solve the structure in these space groups using both direct methods and Patterson techniques consistently failed to give a recognizable solution. Eventually, trial-and-error methods were used to obtain a partial solution in the space group $P\bar{6}2c$, and the calculation of subsequent difference-Fourier maps permitted a structure model to be assembled. However, it became apparent that the correct space-group is not $P\bar{6}2c$, as indicated by very high correlation of atomic positional parameters in the least-squares refinement; we transformed the solution into the space group $P6_3/mmc$, which the successful refinement shows to be the space group of claringbullite. The structure model consists of two Cu atoms at the 6g and 6h (6h is one-third occupied) positions, two Cl atoms at the 2c and 2b positions, and an O atom on the 12k position. Refinement of the positional parameters and an isotropic-displacement model gave an R index of 10.0%. Conversion to an anisotropic-displacement model, together with the refinement of all parameters, converged to an R index of 3.9% and a wR

TABLE 2. ATOMIC AND DISPLACEMENT (x10^4) PARAMETERS FOR CLARINGBULLITE

	x	y	z	$*U_{equiv}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	½	0	0	145(3)	91(3)	88(4)	256(5)	-61(4)	-30(2)	44(2)
Cu(2)	0.3711(2)	0.7422(4)	¾	84(8)	86(9)	124(13)	54(10)	0	0	62(6)
Cl(1)	⅔	⅓	¾	239(11)	235(13)	235(13)	247(18)	0	0	118(7)
Cl(2)	0	0	¾	436(26)	396(30)	396(30)	515(48)	0	0	198(15)
O(1)	0.2017(3)	0.7983(3)	0.9082(4)	105(10)	84(11)	84(11)	138(14)	17(7)	-17(7)	34(12)
H(1)	0.125(2)	0.875(2)	0.868(7)	200						

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR CLARINGBULLITE

Cu(1)ϕ_6 octahedron					
Cu(1)-Cl(1)	2.997(1)	x2			
Cu(1)-O(1)	1.951(2)	x4			
Cl(1)-O(1)	3.662(2)	x4	Cl(1)-Cu(1)-O(1)	93.0(1)	x4
Cl(1)-O(1)	3.489(3)	x4	Cl(1)-Cu(1)-O(1)	87.0(1)	x4
O(1)-O(1)	2.634(2)	x2	O(1)-Cu(1)-O(1)	84.9(1)	x2
O(1)-O(1)	2.878(4)	x2	O(1)-Cu(1)-O(1)	95.1(1)	x2
Cu(2)ϕ_6 trigonal prism					
Cu(2)-O(1)a,b	2.438(3)	x2			
Cu(2)-O(1)	1.988(2)	x4			
O(1)a,b-O(1)	2.634(2)	x4	O(1)a,b-Cu(2)-O(1)	72.3(1)	x4
O(1)a,b-O(1)	3.922(5)	x4	O(1)a,b-Cu(2)-O(1)	124.5(1)	x4
O(1)-O(1)	2.634(2)	x2	O(1)-Cu(2)-O(1)	83.0(1)	x2
O(1)-O(1)	2.906(7)	x2	O(1)-Cu(2)-O(1)	93.9(1)	x2
O(1)a-O(1)b	2.906(7)		O(1)a-Cu(2)-O(1)b	73.2(2)	
hydrogen bonding					
H(1)-O(1)	0.96(3)		H(1)···Cl(2)	1.81(4)	
O(1)-Cl(2)	2.747(2)		O(1)-H(1)-Cl(2)	166(5)	

TABLE 4. BOND-VALENCE* ANALYSIS (v.u.) FOR CLARINGBULLITE

	Cu(1)	Cu(2)	H(1)	Σ
O(1)	$0.482\downarrow^{x4}\rightarrow^{x2}$	$0.436\downarrow^{x4}\rightarrow^{x1/6}$ $0.130\downarrow^{x2}\rightarrow^{x1/6}$	0.83	2.13
Cl(1)	$0.117\downarrow^{x2}\rightarrow^{x6}$			0.70
Cl(2)			$0.17\rightarrow^{x6}$	1.02
Σ	2.162	2.004	1.00	

* parameters from Brown & Altermatt (1985)

index of 3.8%. A three-dimensional difference-Fourier map was calculated at this stage of the refinement. The largest difference peak had a height of 0.96 e/Å^3, and was located near the Cu(1) position. The next-largest difference peak was 0.92 e/Å^3, which was located 0.9 Å from O(1) on a 12k position; a hydrogen atom was assigned to this difference peak. All other peaks in the difference-Fourier map were less than 0.66 e/Å^3. Subsequent cycles of refinement gave a hydrogen position that was not realistic, as indicated by anomalously short donor–hydrogen bond-lengths, a common feature of hydrogen positions refined using X-ray data. The "soft" constraint that the donor–hydrogen distance should be ~0.96 Å was imposed by adding extra weighted observational equations to the least-squares matrix. Only the donor–hydrogen distance is constrained, and the hydrogen position is free to seek its optimum position around the donor atom. Refinement of all parameters gave a final R index of 3.4% and a wR index of 3.2%. Refinements using a structure-factor weighting scheme and an isotropic extinction correction were tried, but neither improved the results of the refinement. Final positional and displacement parameters are given in Table 2, selected interatomic distances and angles in Table 3, and a bond-valence analysis in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

STRUCTURE DESCRIPTION: CATION COORDINATION

Cu(1)ϕ_6 octahedron

The Cu(1) site is octahedrally coordinated by four O(1) anions and two Cl(1) anions. The four O anions are in a square-planar arrangement around the central Cu, with Cu(1)–O(1) distances of 1.951 Å, and the Cl anions form the apices of the distorted octahedron, with Cu(1)–Cl(1) distances of 2.997 Å.

Virtually all $Cu^{2+}O_6$ octahedra observed in minerals and other inorganic compounds are (4 + 2)-distorted owing to the Jahn–Teller relaxation associated with the energetic degeneracy of a d^9 electron configuration in a holosymmetrical octahedral field (Burns 1994, Eby & Hawthorne 1993). In the case of mixed-ligand octahedra [such as Cu(1)ϕ_6 here, ϕ representing an unspecified ligand], it is not possible to have a strictly holosymmetrical octahedral environment around Cu, thus the Jahn–Teller theorem *sensu stricto* does not apply. However, a near-degenerate electronic state may occur, and distortion of the octahedral environment may lead to a significant stabilization. Comparison of the Cu-ϕ bond-lengths of the Cu(1)ϕ_6 octahedron in claringbullite with the (4 + 2)-distorted $CuCl_6$ octahedron in tolbachite (Burns & Hawthorne 1993) and the typical (4 + 2)-distorted geometries of CuO_6 octahedra in various minerals (Burns 1994, Eby & Hawthorne 1993) shows that the Cu(1)ϕ_6 octahedron in claringbullite is significantly (4 + 2)-distorted owing to the Jahn–Teller effect. This is in line with the observation that all Cuϕ_6 mixed-ligand octahedra with four O and two Cl in minerals (there are 15 known) are (4 + 2)-distorted, with the Cl anions always at the apical positions of the distorted octahedron (Burns 1994).

Cu(2)ϕ_6 trigonal prism

The Cu(2) site is a 6*h* position in the space group *P*6_3*/mmc*. Site-scattering refinement indicates that the Cu(2) site is only one-third occupied, and examination of its local geometry shows that clusters of three symmetrically equivalent Cu(2) sites occur, each being separated from the other two by 0.756(3) Å. The 2*d* position, with site symmetry $\bar{6}m2$, is located at the center of the three Cu(2) sites, but a difference-Fourier map (Fig. 1a) calculated with the Cu(2) site vacant clearly shows that the electron density is displaced off the $\bar{6}$ symmetry axis. The one-third occupancy factor obtained for the Cu(2) site is consistent with only one of the three Cu(2) sites being occupied on a local scale.

The Cu(2) site is coordinated by six O(1) anions in the form of a distorted trigonal prism (Fig. 1b). The 2*d* position is at the center of the trigonal prism, and each of the Cu(2) sites is displaced away from the 2*d* position toward one of the prism faces, giving four short Cu(2)–O(1) bonds of 1.988 Å, and two long Cu(2)–O(1) bonds of 2.438 Å (Table 3), with a <Cu(2)–O(1)> bond-length of 2.138 Å. The 2*d* position, which is at the center of the trigonal prism, is 2.102 Å away from the O(1) anions that form the apices of the trigonal prism.

By far the most common six-coordinate geometry is octahedral. The trigonal prism is an alternate arrangement, but it is seldom observed in oxysalt mineral structures. This is probably due to the fact that ligand separations are smaller in the trigonal prism than in the octahedron; thus the octahedral geometry will have a lower energy unless ligand interaction is favorable, as is the case in some MS_2 structures with M in trigonal prismatic coordination. In Cu^{2+} oxysalt minerals, the distorted octahedral arrangement of ligands around Cu^{2+} is dominant. However, in addition to claringbullite, there are three other minerals that contain Cu^{2+} in trigonal prismatic coordination: the Cu(3) site in buttgenbachite, $Cu_{18}(NO_3)_2(OH)_{32}Cl_3{\cdot}H_2O$ (Fanfani *et al.* 1973), the Cu(3) site in connellite, $Cu_{19}Cl_4SO_4(OH)_{32}{\cdot}3H_2O$ (McLean & Anthony 1972), and the Cu(2) site in lyonsite, $Cu_3Fe_4(VO_4)_6$ (Hughes *et al.* 1987). In each of these cases, the trigonal prism is distorted in a way similar to that observed in claringbullite. There are four short bonds to anions on one side of the Cu atom, and longer bonds to two anions on the other side of the Cu atom. In all cases, the four short bonds are of similar length. However, considerable variation occurs in the longer bonds: Cu(3) in buttgenbachite bonds to two (OH) anions at 2.910 Å, with a bond angle of 58.0°, Cu(3) in connellite bonds to two (OH) anions at 2.875 Å, with a bond angle of 59.2°, and Cu(2) in lyonsite bonds to two O anions at 2.576 Å, with a bond angle of 82.2°.

STRUCTURE DESCRIPTION: CONNECTIVITY AMONG POLYHEDRA

The most striking feature of the claringbullite structure is the sheet of edge-sharing octahedra parallel to (001) (Fig. 2). The sheet contains $Cu(1)(OH)_4Cl_2$ mixed-ligand edge-sharing octahedra, and has a composition $Cu(1)_3(OH)_6Cl_2$. The sheet is similar to the sheet of octahedra in botallackite (Hawthorne 1985) except that 25% of the octahedral sites are vacant. The holes in the sheet of octahedra are significantly larger than would be expected if the sheets were constructed

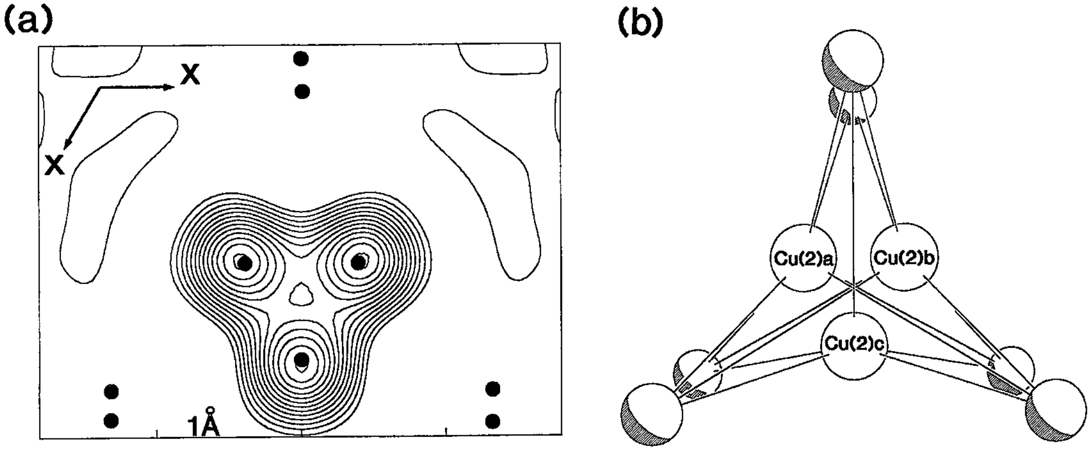

FIG. 1. The Cu(2)ϕ_6 trigonal prism in claringbullite. (a) Difference-Fourier map calculated around the Cu(2) site with that site vacant. Contour interval = 2 e/Å^3; (b) the Cu(2)ϕ_6 trigonal prism; note that each of the Cu(2) sites is only occupied in one-third of the cases.

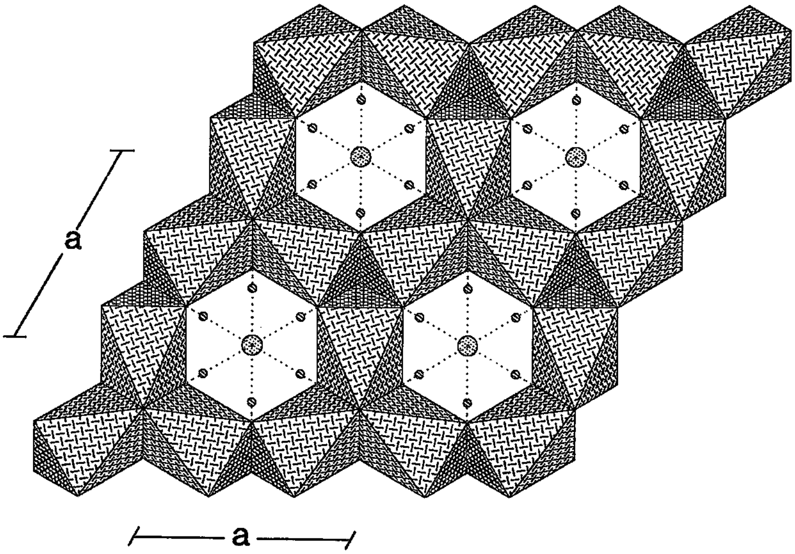

FIG. 2. The structure of claringbullite projected down [001]; the Cu(1)ϕ_6 octahedra are shaded with a herring-bone pattern, Cl(2) atoms are shown as circles shaded with a random-dot pattern, and H atoms are small circles shaded with parallel lines; hydrogen bonds are shown as dotted lines.

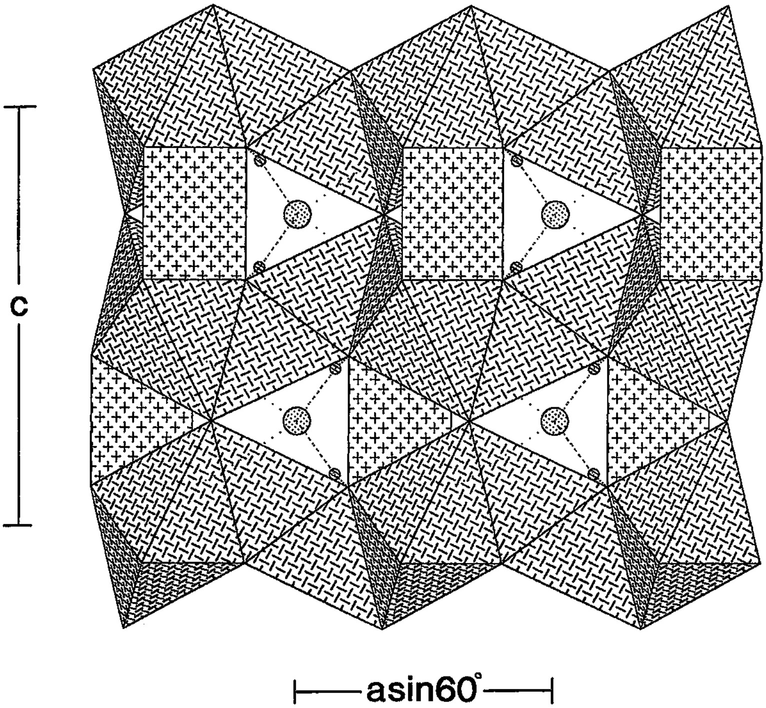

FIG. 3. The structure of claringbullite projected down [100]; legend as in Figure 2. The Cu(2)ϕ_6 trigonal prisms are shaded with crosses.

from holosymmetrical octahedra; the Jahn–Teller effect distorts the Cu(1)ϕ_6 octahedron, resulting in a distortion of the sheets of octahedra, and giving a hole ~4.0 Å in diameter.

The sheets of octahedra are stacked along [001] such that the holes of adjacent sheets are collinear, resulting in channels through the structure parallel to [001]. A projection of the claringbullite structure down [100] reveals that it is a framework structure (Fig. 3). Adjacent sheets of [Cu(1)$_3\phi_8$] octahedra share Cl ligands along [001], giving a [Cu(1)$_3$(OH)$_6$Cl] framework. The Cu(2) site occurs between the sheets of octahedra, at a point where the stacking of sheets provides trigonal prismatic coordination (Figs. 1b, 3). The Cu(2)(OH)$_6$ trigonal prism contains three ligands from adjacent sheets of octahedra, and the Cu(2) position is thus a part of the framework of the structure. The composition of this framework is [Cu(1)$_3$Cu(2)(OH)$_6$Cl]$^{1+}$, with a single positive charge. To satisfy the electroneutrality principle, an additional anion is required. The Cl(2) position is at the center of the channel (Fig. 2), at a point midway between adjacent sheets of octahedra (Fig. 3). The Cl(2) anion accepts a total of six hydrogen bonds, three from donor anions in each adjacent sheet (Fig. 3).

THE CHEMICAL FORMULA OF CLARINGBULLITE

Fejer *et al.* (1977) gave the chemical formula of claringbullite as $Cu_4Cl(OH)_7 \cdot nH_2O$ with $n \approx ½$, $Z = 2$. This formula gives a calculated density of 3.92 g/cm^3, in good agreement with the measured density of 3.9 g/cm^3. This structure determination shows that there are two Cu sites, at the 6*g* and 6*h* positions, and the Cu(2) site is one-third occupied (see above), giving a total of eight Cu atoms per unit cell. Site-scattering refinements are consistent with these two sites containing only Cu. The structure has two Cl sites, at the 2*c* and 2*b* positions. Site-scattering refinement shows that the Cl(1) site is occupied by Cl only, giving two Cl atoms per unit cell. The occupancy factor for the Cl(2) site refined to a value well below the ideal value for full occupancy by Cl, indicating substitution of another species or a vacancy at this site. The electroneutrality principle suggests that the substituting species is a monovalent anion, and (OH)$^-$ is a likely candidate. A constrained site-occupancy refinement indicates that the site is approximately 29% Cl and 71% (OH), giving 0.58(7) Cl and 1.42(7) (OH) per unit cell. Finally, the O(1) and H(1) sites are at 12*k* positions, giving twelve (OH) groups per unit cell. Difference-Fourier maps calculated during the latter stages of refinement do not show any electron density attributable to hydrogen-bonded (H_2O). Thus the formula for the claringbullite sample studied here is $Cu_4Cl[Cl_{0.29}(OH)_{0.71}](OH)_6$, $Z = 2$, which gives a calculated density of 3.882 g/cm^3.

The Cl(2) site is occupied by $Cl_{0.29}(OH)_{0.71}$; there seems no reason why there should not be complete Cl ↔ OH solid solution at this site, with end-members $Cu_4(OH)_7Cl$ and $Cu_4(OH)_6Cl_2$. The latter may be rewritten as $Cu_2(OH)_3Cl$, which is the formula of botallackite (and its polymorphs atacamite and paratacamite). Thus there is the possibility of a fourth polymorph for the $Cu_2(OH)_3Cl$ composition.

RELATION TO OTHER SPECIES

We write a simplified formula of claringbullite as $Cu_4\phi_8$ (= [Cuϕ_2]$_4$), where ϕ is an unspecified anion. There are several copper minerals of this specific stoichiometry (Table 5), and the relationship of claringbullite to these is of particular interest. Spertiniite, botallackite and tolbachite each have a structural unit based on a brucite-like [Mϕ_2] sheet of edge-sharing octahedra. Despite the fact that we may write a general formula for these minerals as Cuϕ_2, ϕ = (OH,Cl), there does not seem to be an extensive solid-solution between OH and Cl in these structures. In addition, the specific structural arrangement adopted seems to be a result of the need for Cu^{2+} to have a (4 + 2)-distorted octahedral coordination, the relative site-preferences of Cl and OH in (4 + 2)-distorted Cu$^{2+}\phi_6$ octahedra, and the requirement that the octahedra articulate completely in the [Mϕ_2] sheet. Consideration of these three factors suggests that the structure of claringbullite can *not* be based on an [Mϕ_2] sheet, despite the well-developed (001) cleavage and the indication of the formula; it was this dichotomy that prompted our study of claringbullite. This intuition turned out to be correct. The structure of claringbullite is not based on an [Mϕ_2] sheet; instead it has a rather exotic atomic arrangement of its own.

Instead of an [Mϕ_2] sheet, claringbullite has an [M$_3\square\phi_8$] sheet similar to the [Al$_4$Zn$\square\phi_{12}$] sheet in alvanite (Pertlik & Dunn 1990). The composition of the sheet, $Cu^{2+}_3(OH)_6Cl_2$, allows the Cl to constitute the apical ligands of the typical (4 + 2)-distorted Cuϕ_6 octahedron, and the connectivity of the octahedra allows the sheet to dilate relative to the analogous arrangement of holosymmetrical octahedra while retaining its connectivity. This dilation forms unusually large octahedral "holes" in the sheet (Fig. 2), at the

TABLE 5. COPPER MINERALS OF Cuϕ_2 STOICHIOMETRY

atacamite	$Cu_2(OH)_3Cl$
botallackite	$Cu_2(OH)_3Cl$
claringbullite	$Cu_4Cl[Cl_{0.29}(OH)_{0.71}](OH)_6$
paratacamite	$Cu_2(OH)_3Cl$
spertiniite	$Cu(OH)_2$
tolbachite	$CuCl_2$

center of which occurs the remaining anion site. Note that the constitution of the sheet, $Cu^{2+}_3(OH)_6Cl_2$, suggests that all the anions are already accounted for. However, the sheets are joined in the *z* direction by sharing apical Cl atoms (Fig. 3), forming a weakly bonded framework of the form $Cu_3\square(OH)_6Cl$. The charge on this framework is 1^- per formula unit (*pfu*). The incorporation of Cu^{2+} into the framework is required to satisfy the bond-valence requirements of the equatorial OH anions of the $Cu(1)\phi_6$ octahedra, and hence there must be one additional Cu^{2+} *pfu* to link to all of the OH anions. This produces an excess charge of 1^+, which is balanced by the incorporation of (OH,Cl) in the octahedral holes of the sheet (Fig. 2).

Why is the linking Cu^{2+} between the $[Cu^{2+}_3\square(OH)_6Cl_2]$ sheets in trigonal prismatic coordination? This coordination is forced by the requirement, discussed above, that adjacent sheets of octahedra share apical Cl atoms. Where this linkage occurs, the Cu^{2+} coordination between the sheets is trigonal prismatic; if adjacent sheets are rotated 60° to achieve octahedral coordination around the intersheet Cu^{2+}, the apical Cl atoms no longer line up to allow intersheet linkage, and the stoichiometry and electroneutrality requirements of the structure are violated. Thus we can understand the unusual atomic arrangement in the claringbullite structure as a result of the need to incorporate the specific anion composition into a structure of the form $[M\phi_2]$.

ACKNOWLEDGEMENTS

We are indebted to Mr. Forrest Cureton for providing the specimen of claringbullite used in this work. The Natural Sciences and Engineering Research Council of Canada provided support with Operating, Infrastructure and Major Equipment grants to FCH. The clarity and quality of this contribution were enhanced by the efforts of two anonymous referees and the editorial work of Dr. R.F. Martin.

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Received April 11, 1994, revised manuscript accepted October 12, 1994.