American Mineralogist
Vol. 57, pp. 426–438 (1972)

THE DISORDERED, "ZEOLITE-LIKE" STRUCTURE OF CONNELLITE[1]

W. JOHN MCLEAN AND JOHN W. ANTHONY, *Department of Geosciences, University of Arizona, Tucson, Arizona 85721*

ABSTRACT

The crystal structure of connellite has been solved from the Patterson function and refined to an R factor of 0.07. The structure analysis shows the most probable space group to be $P\bar{6}2c$. The most probable chemical composition of the crystal studied is:

$$Cu_{36.8}[(SO_4)_{.8}, (NO_3)_{.2}]_2Cl_6(OH)_{60}[Cl_{.33}, (OH)_{.33}, (H_2O)_{.33}]_6 \cdot 6H_2O$$

The structure consists of an intricate three-dimensional framework which contains large channels parallel to the c axis. In overall aspect, however, the structure is geometrically simple. The framework is composed of edge and corner-sharing polyhedra with Cu^{2+} as the central ion and apices composed of $(OH)^-$, Cl^-, and H_2O. The polyhedra are, with one exception, distorted octahedra. The channel contains the disordered SO_4 ion. The disorder is the result of the tetrahedral SO_4 filling a $\bar{6}$ site and an apparent one for one substitution of NO_3 for SO_4.

INTRODUCTION

The mineral named connellite by Dana in 1850 is known from many localities in Europe, Africa, and North America, but its chemical and crystallographic definition is deficient in some aspects. Several chemical analyses of connellite are reported (Palache, Berman, and Frondel, 1951) which, in aggregate, suggest the composition $Cu_{19}(SO_4)Cl_4(OH)_{32} \cdot 3H_2O$. Buttgenbachite (Schoep, 1925) has been assigned the analogous formula $Cu_{19}(NO_3)_2Cl_4(OH)_{32} \cdot 3H_2O$ and may form a complete solid solution series with connellite. The unit cell of connellite has been recognized (Donnay *et al.*, 1963) as being incorrectly given in *Dana's System of Mineralogy* (Palache *et al.*, 1951), but application of the correct parameters shows that there are two formula units per cell. The space group was reported in *Dana's System* to be probably $C6_3/mmc$ ($P6_3/mmc$, $P6_3mc$, or $P\bar{6}2c$). The presence of 38 Cu, two (SO_4), eight Cl, and 64 (OH) per unit cell in any of these hexagonal space groups is improbable and leads to the supposition that either the space group or the composition given above is incorrect, or that the crystal structure is disordered. The structure of connellite shows that the latter is the case. The most probable space group is $P\bar{6}2c$ and the chemical analyses are surprisingly good.

---

[1] Contribution No. 26 from the Department of Geosciences, University of Arizona.

EXPERIMENTAL

Crystals of connellite from the Toughnut mine, Tombstone, Arizona (University of Arizona, Mineralogical Museum specimen no. 26) were ground to spheres and a sphere .016 mm in diameter was selected for data collection. Weissenberg photographs show the unit cell and space group to be $a = 15.78$ Å, $c = 9.10$ Å, and $P6_3mc$ (No. 186), $P\bar{6}_2c$ (No. 190), or $P6_3/mmc$ (No. 194). With the composition assumed to be $Cu_{19}(SO_4)Cl_4(OH)_{32} \cdot 3H_2O$, $Z = 2$ and the calculated density is 3.46 gm/cm³, which compares with the measured specific gravity of 3.36 (Palache *et al.*, 1951). Intensity data were collected manually on a Supper diffractometer of Weissenberg geometry and 641 independent reflections were measured of which 493 were strong enough to be considered as observed. The intensities were corrected for absorption by linear interpolation of the spherical corrections taken from the *International Tables for X-Ray Crystallography*, Vol. II, pp. 304 and 305, with a μR value of 1.15.

STRUCTURE DETERMINATION

A Patterson synthesis was calculated and routinely solved for 36 copper atoms per unit cell. The analysis of the Patterson did not distinguish the space group from among the three possible groups. Because the required SO_4 ions could be accommodated within it without disorder, space group $P6_3mc$ was initially assumed and produced an R factor of 0.37. A series of difference syntheses added $Cl_6(OH)_{66}S_2$ to the unit cell with the $Cu_{36}Cl_6(OH)_{66}$ part of the structure forming a three-dimensional

Table 1. Comparison of Analyses of Connellite

	1	2	3	4
CuO	73.96	73.38	73.22	73.11
SO_3	3.92	3.15	3.20	3.98
N_2O_5	–	.72	.54	–
Cl	6.94	6.82	7.09	7.05
H_2O	16.75	17.13	17.55	17.45
	101.57	101.20	101.60	101.59
O = Cl	1.57	1.53	1.60	1.59
	100.00	99.67	100.00	100.00

1. $Cu_{38}(SO_4)_2Cl_8(OH)_{64} \cdot 6H_2O$
2. Connellite. Czar Mine, Bisbee (Ford and Bradley, 1915)
3. $Cu_{36.8}[(SO_4)_{.8},(NO_3)_{.2}]_2Cl_6(OH)_{60}[Cl_{.33},(OH)_{.33},(H_2O)_{.33}]_6 \cdot 6H_2O$
4. $Cu_{37}(SO_4)_2Cl_8(OH)_{62} \cdot 8H_2O$

Table 2. Atomic Parameters for Connellite

Atom	x	y	z	B	Occupancy
Cu(1)	.2032(6)	.0000	.5000	1.1(2)	0.5
Cu(1A)[b]	.7986(7)	.0000	.5000	1.3(2)	0.5
Cu(2)	.3595(8)	.0149(9)	.2500	1.6(2)	0.5
Cu(2A)[b]	.3591(8)	.3415(8)	.2500	0.8(2)	0.5
Cu(3)	.3349(3)	.1678(10)	.7500	1.2(1)	0.5
Cu(4)	.5012(9)	.0000	.5000	1.2(1)	0.5
Cu(5)	.0000	.0000	.0000	1.26[c]	0.048(3)
Cl	.2767(5)	.1418(21)	.2500	0.9(1)	0.5
O(1)	.451(2)	.077(2)	.092(5)	0.5(6)	1.0
O(1A)[b]	.450(2)	.366(2)	.088(4)	0.2(6)	1.0
O(3)	.324(3)	.067(3)	.615(4)	0.0(6)	1.0
O(3A)[b]	.329(3)	.254(2)	.599(4)	0.9(6)	1.0
O(5)	.152(1)	.080(3)	.594(2)	1.8(3)	1.0
O(7)	.562(4)	.451(4)	.750	1.8[c]	0.333
Cl(7)	.562[c]	.451[c]	.750	1.8[c]	0.167
S	.6667	.3333	.2500	2.0[c]	0.133
O(8)	.636[c]	.268[c]	.1184[c]	2.5[c]	0.267
O(9)	.622[c]	.396[c]	.250	2.5[c]	0.133
O(10)	.775[c]	.396[c]	.250	2.5[c]	0.133
N	.6667	.3333	.2500	2.0[c]	0.034
O(11)	.622[c]	.244[c]	.250	2.5[c]	0.100
O(12)	.512(3)	.258(10)	.695(4)	5.6(10)	0.5

[a] Numbers in parentheses are standard errors and refer to the last places.

[b] Atom would be equivalent to the preceding atom if the space group were $P6_3/mmc$.

[c] Parameter not refined because of disorder.

framework and the sulfur occupying channels along one of the 6_3 axes. Full matrix least squares refinement reduced R to 0.21.

The sulfate oxygen atoms were not present in the expected positions in the difference syntheses and calculations were shifted to space group $P31c$ which contains only symmetry common to the three groups $P6_3/mmc$, $P6_3mc$, and $P\bar{6}2c$. Refinement by least squares and difference synthesis indicated the positions of the sulfate oxygens, a partly occupied Cu site at the origin, and an apparent water molecule in a 6-fold position which appeared to be disordered in concert with the disorder of the sulfate group. These additions reduced R to 0.068. The ordered atoms were manually shifted back to their symmetry-required positions in the three possible space groups. Isotropic least squares refinement produced a lowest R of 0.065 in space group $P\bar{6}2c$ and various criteria including those of Hamilton (1965) indicate that $P\bar{6}2c$ is the most probable space group, although the deviation from $P6_3/mmc$ is very small. Difference map residuals at the O(7) position indicated substitution of a heavier atom (Cl) for oxygen and disorder which was synchronous with the disorder of the sulfate. Residuals in the region of the sulfate were interpreted as indicating a substitution of about 20 percent NO_3 for SO_4. Substitutions of about this magnitude have been found in connellite analyses (Ford and Bradley, 1915). If one assumes substitution of Cl for 1/3 of the oxygens in the O(7) site and substitution of 20 percent NO_3 for SO_4, the composition of connellite can be written:

$$Cu_{36.8}[(SO_4)_{.8},(NO_3)_{.2}]_2Cl_6(OH)_{60}[Cl_{.33},(OH)_{.67}]_6\cdot 6H_2O.$$

Such a composition does not provide charge balance, but it can be obtained by substitution of two waters for two hydroxyls per cell. Speculatively, one might assume this substitution to occur in the already disordered O(7) site. This would give:

$$Cu_{36.8}[(SO_4)_{.8},(NO_3)_{.2}]_2Cl_6(OH)_{60}[Cl_{.33},(OH)_{.33},(H_2O)_{.33}]_6\cdot 6H_2O$$

as the most reasonable composition derivable from the crystal structure analysis. The ideal connellite end member would presumably have a composition of: $Cu_{37}(SO_4)_2Cl_8(OH)_{62}\cdot 8H_2O$ which differs only slightly from the original composition of: $Cu_{38}(SO_4)_2Cl_8(OH)_{64}\cdot 6H_2O$. Theoretical analyses derived from the above compositions are compared with the nitrate-bearing connellite analysis of Ford and Bradley (1915) in Table 1. The density calculated from the structure-derived composition is 3.384 compared to 3.36 measured and 3.46 calculated from the original composition.

Final atomic parameters are in Table 2. Table 3 contains the observed and calculated structure factors.[1] Atomic scattering factors were for atoms of Cu, S, O, and N, and for the Cl^- ion taken from the *International Tables for X-Ray Crystallography*, Vol. III, pp. 202–205.

DESCRIPTION OF THE STRUCTURE

The ordered part of the structure of connellite is very unusual for compounds of its type. It consists of an elegant, three-dimensional, ionic-covalently bonded framework which contains *large channels* as shown in Figure 1.

The framework is composed of Cu^{2+} ions which are, with one exception, 6-fold coordinated by $(OH)^-$ and Cl^- ions and H_2O molecules. The 6-fold coordination polyhedra are of generally octahedral configuration, but are characteristically distorted because of the Jahn-Teller effect. The resulting shape is that of an elongate tetragonal dipyramid. Additional distortion occurs when the large Cl^- ion takes part in a polyhedron. The details of the Cu polyhedra may be obtained by

---

[1] To obtain a copy of Table 3, order NAPS Document No. 01712 from National Auxiliary Publications Service of A.S.I.S., c/o CCM Information Corporation, 866 Third Avenue, New York, N.Y. 10022, remitting in advance $2.00 for microfiche or $5.00 for photocopies payable to CCMIC-NAPS.

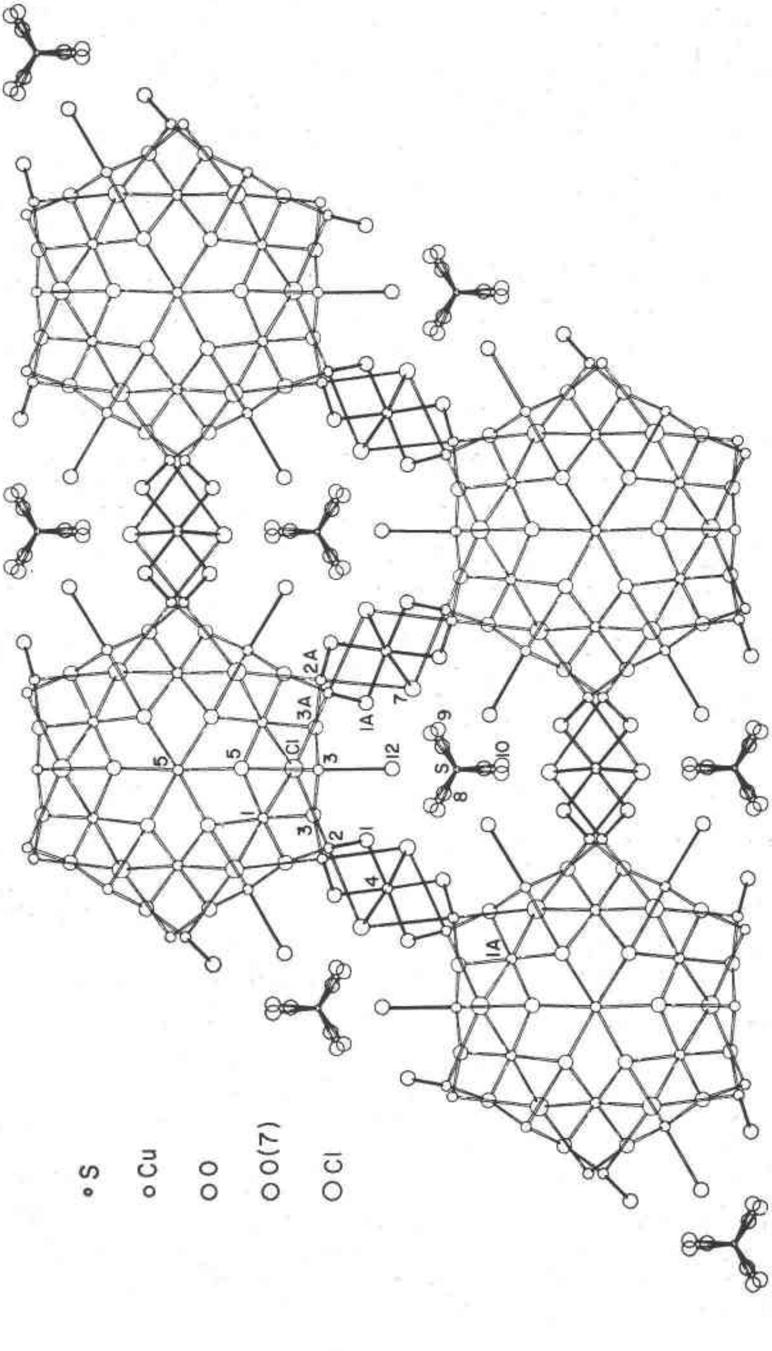
S
Cu
O
O(7)
Cl
2A
3A
1A
7
Cl
5
5
3
12
9
S
10
8
1
3
2
1
4
1A

Table 4. Interatomic Distances and Angles in Connellite

Distances

i	j	d_{ij}
Cu(1)	Cl	2.99(1) Å
Cu(1)	O(3)	1.95(4)
Cu(1)	O(5)	2.00(3)
Cu(1A)	Cl	2.93(1)
Cu(1A)	O(3A)	1.97(4)
Cu(1A)	O(5)	1.88(3)
Cu(2)	Cl	2.89(3)
Cu(2)	O(7)	2.99(7)
Cu(2)	O(1)	1.93(4)
Cu(2)	O(3)	1.93(4)
Cu(2A)	Cl	2.74(3)
Cu(2A)	O(7)	3.03(7)
Cu(2A)	O(1A)	1.96(4)
Cu(2A)	O(3A)	2.08(4)
Cu(3)	O(12)	2.47(8)
Cu(3)	O(5)	2.87(3)
Cu(3)	O(3)	1.95(4)
Cu(3)	O(3A)	1.97(4)
Cu(4)	O(7)	2.74(3)
Cu(4)	O(1)	1.94(4)
Cu(4)	O(1A)	2.00(4)
Cu(5)	O(5)	2.25(3)

Angles

i	j	k	Angle_{ijk}
Cl	Cu(1)	Cl	178(0)°
O(3)	Cu(1)	O(5)	172(1)

Angles

i	j	k	Angle_{ijk}
Cl	Cu(1)	O(3)	95(1)°
Cl	Cu(1)	O(3)	83(1)
Cl	Cu(1)	O(5)	89(1)
Cl	Cu(1)	O(5)	92(1)
O(3)	Cu(1)	O(5)	91(1)
O(3)	Cu(1)	O(3)	91(2)
O(5)	Cu(1)	O(5)	88(1)
Cl	Cu(1A)	Cl	175(0)
O(3A)	Cu(1A)	O(5)	180(1)
Cl	Cu(1A)	O(3A)	90(1)
Cl	Cu(1A)	O(3A)	87(1)
Cl	Cu(1A)	O(5)	93(1)
Cl	Cu(1A)	O(5)	90(1)
O(3A)	Cu(1A)	O(5)	92(1)
O(3A)	Cu(1A)	O(3A)	88(2)
O(5)	Cu(1A)	O(5)	88(1)
Cl	Cu(2)	O(7)	178(1)
O(1)	Cu(2)	O(3)	170(2)
Cl	Cu(2)	O(1)	97(1)
Cl	Cu(2)	O(3)	87(1)
O(7)	Cu(2)	O(1)	81(1)
O(7)	Cu(2)	O(3)	95(1)
O(1)	Cu(2)	O(3)	79(2)
O(1)	Cu(2)	O(1)	97(2)
O(3)	Cu(2)	O(3)	92(2)
Cl	Cu(2A)	O(7)	180(1)
O(1A)	Cu(2A)	O(3A)	170(2)
Cl	Cu(2A)	O(1A)	96(1)
Cl	Cu(2A)	O(3A)	90(1)
O(7)	Cu(2A)	O(1A)	84(1)
O(7)	Cu(2A)	O(3A)	91(1)

Angles

i	j	k	Angle_{ijk}
O(1A)	Cu(2A)	O(3A)	90(2)°
O(3A)	Cu(2A)	O(1A)	98(2)
O(3A)	Cu(2A)	O(3A)	82(2)
O(3)	Cu(3)	O(3A)	172(2)
O(3)	Cu(3)	O(3A)	96(2)
O(3)	Cu(3)	O(3)	78(2)
O(3A)	Cu(3)	O(3A)	88(2)
O(5)	Cu(3)	O(5)	59(1)
O(3)	Cu(3)	O(5)	69(1)
O(3)	Cu(3)	O(5)	105(1)
O(3A)	Cu(3)	O(5)	67(1)
O(3A)	Cu(3)	O(5)	107(1)
O(12)	Cu(3)	O(5)	139(2)
O(12)	Cu(3)	O(5)	162(2)
O(12)	Cu(3)	O(3)	88(2)
O(12)	Cu(3)	O(3)	102(2)
O(12)	Cu(3)	O(3A)	84(2)
O(12)	Cu(3)	O(3A)	100(2)
O(7)	Cu(4)	O(7)	175(1)
O(1)	Cu(4)	O(1A)	177(2)
O(7)	Cu(4)	O(1)	91(2)
O(7)	Cu(4)	O(1)	85(2)
O(7)	Cu(4)	O(1A)	91(1)
O(7)	Cu(4)	O(1A)	93(1)
O(1)	Cu(4)	O(1A)	92(2)
O(1)	Cu(4)	O(1)	88(2)
O(1A)	Cu(4)	O(1A)	89(2)
O(5)	Cu(5)	O(5)	177(1)
O(5)	Cu(5)	O(5)	106(1)
O(5)	Cu(5)	O(5)	76(1)

[a] Numbers in parentheses are standard errors and refer to the last places.

examination of the interatomic distances and angles within these polyhedra which are listed in Table 4. The Cu(1) and Cu(1A) polyhedra would be identical in $P6_3/mmc$. They contain $4(OH)^-$ and $2Cl^-$ as apices with the Cl^- ions occupying opposite apices. Cu(2) and Cu(2A) also would be identical in $P6_3/mmc$ and are coordinated by $4(OH)^-$, one Cl^-, and the disordered O(7) position which appears to be occupied by Cl^- as well as by $(OH)^-$ and perhaps H_2O. The Cl^- and O(7) form opposite apices. The exception to octahedral configuration occurs with Cu(3) which is 7-fold coordinated by $6(OH)^-$ and O(12). Four of the

←

FIG. 1. The crystal structure of connellite viewed parallel to the *c*-axis with a_1 down and 30° to the left and a_2 to the right. Structure viewed in projection illustrating its intrinsic simplicity. More than one cell is shown with narrow channels at (0, 0, *z*) and large channels at (1/3, 2/3, *z*) and (2/3, 1/3, *z*). Atom numbers are given on the drawing and correspond to the numbering system used throughout.

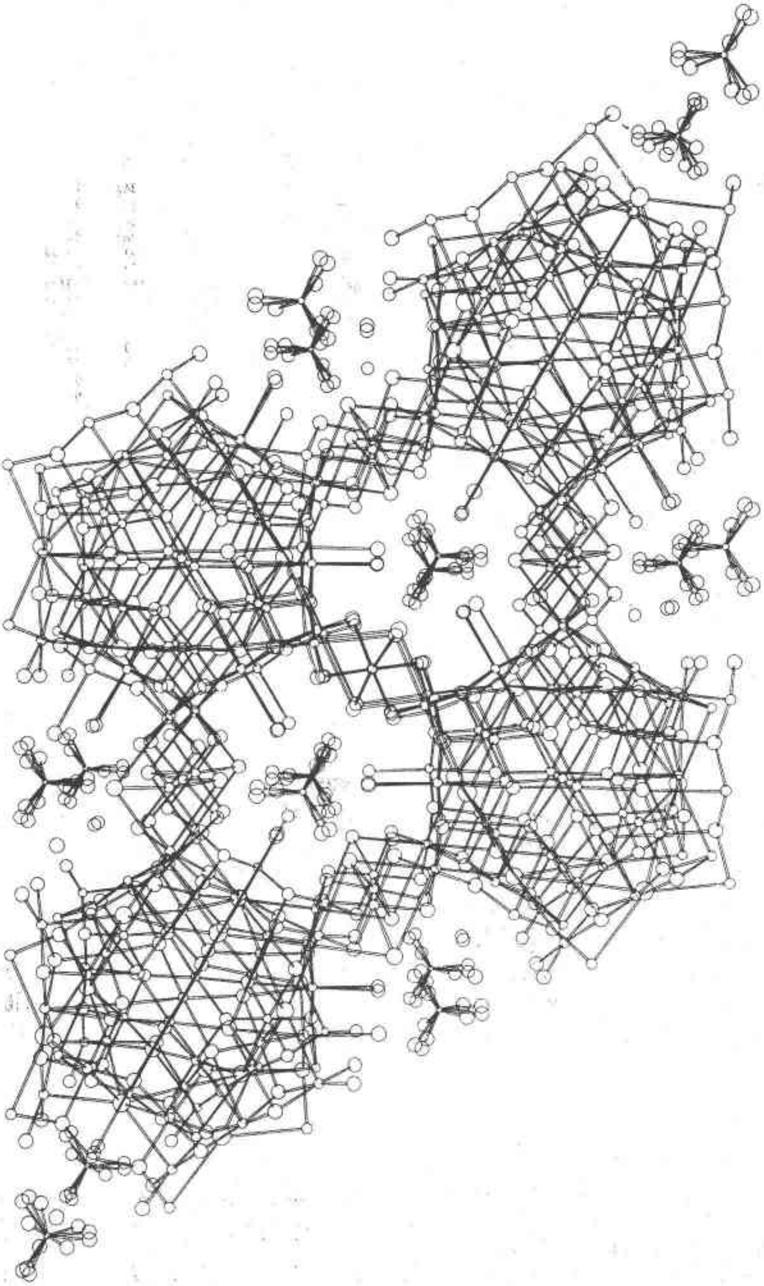

FIG. 2. Structure as in Fig. 1 viewed in perspective illustrating its intricacy when considered in detail.

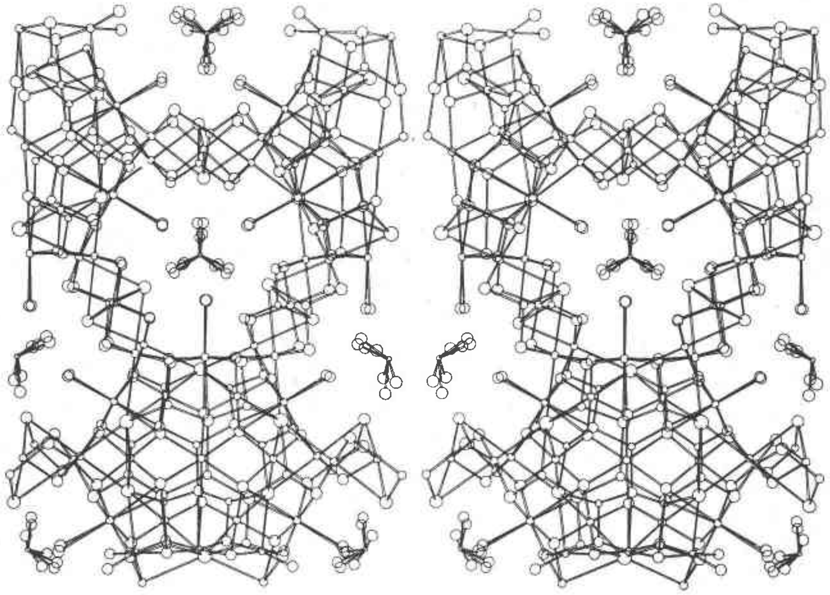

FIG. 3. Structure as in Fig. 1 viewed in stereo illustrating the blend of intricate detail and overall simplicity that is connellite. Shown are one complete narrow channel (1, 1, *z*) and one complete large channel (1/3, 2/3, *z*).

hydroxyl ions form a nearly square plane with Cu(3) at its center. The remaining two hydroxyls lie at about 2.9 Å from the Cu(3) and, with the other four, comprise what may be described as a "pup tent" configuration or, alternatively, a dome. The base of the "pup tent" faces into the channel where the Cu(3) is additionally coordinated by the disordered O(12) which may be a water molecule. The Cu(4) polyhedron resembles those coordinating Cu(1) and Cu(2) in that it has four $(OH)^-$ in a nearly square plane and two more distant apices, in this case formed by O(7). The Cu(5) polyhedron, which is only partly occupied, is a peculiarly distorted octahedron. The distortion takes the form of considerable flattening along one of the $\bar{3}$ axes of the octahedron to produce a polyhedron of trigonal ($\bar{3}2/m$) point symmetry which may be described as approximating a trigonal antiprism, the trigonal axis of which is parallel to *c*.

All the polyhedra except that of Cu(5) contain approximately square planar arrangements of hydroxyls about the Cu^{2+} ion. The Cu–O distances in these polyhedra range from 1.88 to 2.08 Å with a mean for twelve such distances of 1.964 Å. The Cu–Cl bond in the Cu(1) and Cu(2) polyhedra ranges in length from 2.74 to 2.99 Å with a mean

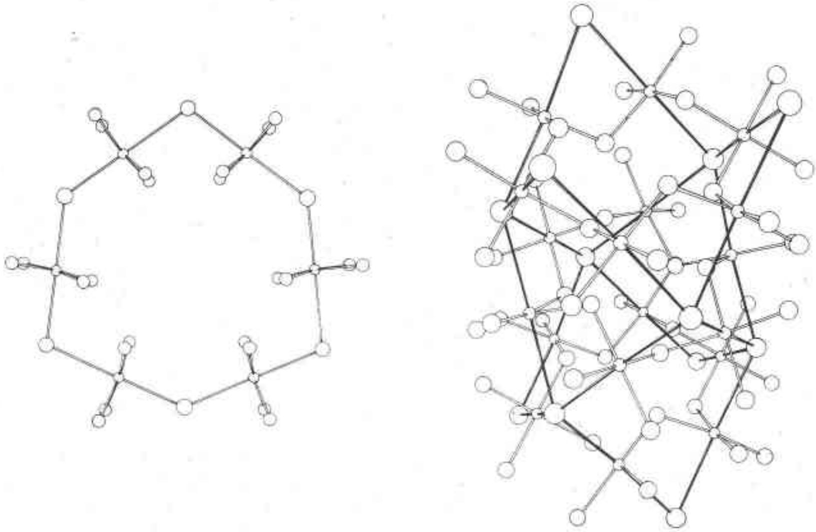

FIG. 4. Structural elements in connellite. A. Ditrigonal ring composed of Cu(2) and Cu(2A) polyhedra. The more obtuse angles of the ring are at Cl and the less obtuse at O(7). View direction is parallel to *c*. B. Cylindrical diamond-shaped network in the structure of connellite composed of Cu(1) and Cu(1A) polyhedra. Cu–Cl bonds are stressed to accent the diamond shape formed by the long axes of the polyhedra. View direction is at 45° to the *c* axis.

of 2.911 Å. This distance presumably takes into account both the large size of the Cl^- ion and the Jahn-Teller distortion. The mean Cu–O(7) distance is 2.873 Å, not significantly smaller than the Cu–Cl distance. This observation might lead one to speculate that there is more than 1/3 Cl^- in the O(7) position. The apparent positional disorder in this site precludes a conclusive denial of such a speculation.

A comparison of the environment of O(7) to that of Cl^- and the other oxygen positions shows that Cl is 6-fold coordinated by Cu while O(3), O(4), and O(5) are 3-fold and O(1), O(1A), O(2), and O(2A) are 2-fold coordinated by Cu^{2+} ions. However, the last four oxygens are located in proximity to the sulfate (2.9 — 3 Å) and presumably may be donors for hydrogen bonding. In contrast to Cl and O, the O(7) site is 4-fold coordinated by Cu which is taken as an indication of a 1/3 (Cl):2/3 (O) substitution in this site.

Cu polyhedra are linked by corner and edge sharing into a framework which is continuous in three dimensions. The dominant feature of the framework is a large channel which parallels the *c* axis and surrounds one of the two unique $\bar{6}$ axes of space group $P\bar{6}2c$. The channel becomes slightly constricted once per *c* periodicity and is widest halfway between constrictions. At its narrowest point the distance from the axis of the channel to the framework (the O(7) site) is 3.04 Å, while at its widest it is 3.70 Å from the axis to the O(2) position. The widest part of the channel is occupied by the disordered sulfate ion. The other $\bar{6}$ axis passes through a much narrower channel. The channels and their disordered occupants will be discussed more fully later.

One of the most conspicuous structural elements is a ditrigonal ring consisting of six apex-sharing Cu(2) polyhedra which encircles the large channel at its widest part (shown in Figure 2A). The shared apices are alternately Cl and O(7) with the more obtuse angles of the ring at Cl and the less obtuse at O(7). Each such ring is linked to three similar rings above and three below encircling the three adjacent channels. The linkage is provided by the polyhedra of Cu(1) and Cu(4), both of which are oriented with their long axes sloping at about 30-40 degrees to the *c* axial direction. Two Cu(4) polyhedra share each O(7) position with two Cu(2) polyhedra of a ring, and the Cu(4) polyhedra form a kinky chain parallel to the *c* axis with each kink bonded to a ring. Four Cu(1) polyhedra share each Cl with two Cu(2) polyhedra of a ring, and each of the four is linked above or below to a different ring which surrounds an adjacent large channel. The convergence of four Cu(1) polyhedra at each Cl position produces a diamond-shaped network which is rounded into the form of a cylinder enclosing the narrow channel, as shown in Figure 2B. Centered in each of the diamonds of the network is the "pup-tent" polyhedron of Cu(3). The narrow channel consists of a series of

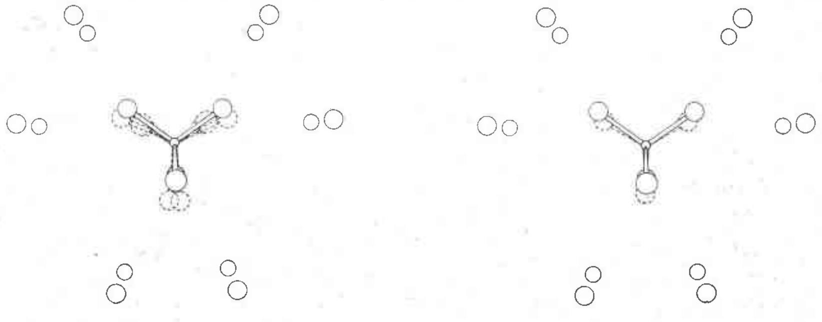

FIG. 5. The sulfate disorder in connellite. A. Three-fold disorder resulting from the occupation of a $\bar{6}$ site by the less symmetrical $(SO_4)^{2-}$ ion. One of the three orientations is indicated by full lines and the alternative orientations by dashed lines. B. Substitutional disorder resulting from the substitution of $(NO_3)^-$ for $(SO_4)^{2-}$. One of the three sulfate orientations is shown by full lines and the superimposed nitrate by dashed lines.

alternating trigonal prisms and trigonal antiprisms. The sites within the trigonal antiprisms are partially occupied by Cu(5) which acts to block the channelway. The narrow channel and enclosing network is one of the most obvious elements of the structure.

The aggregate of these structural elements, the ditrigonal rings and large channels supported and surrounded alternately by three kinky chains and three cylindrical diamond-shaped networks, forms a simple yet intricate geometrical framework which is so elegant and beautiful as to rival any we have seen described. The framework has no obvious directions of weakness and it is not surprising that cleavage is not reported for connellite.

Discussion

The disorder in connellite appears to be of two kinds, statistical disorder of position and disorder caused by substitution. The disorder of the sulfate involves both kinds. Difference map evidence indicates that the sulfate group is oriented so that two of the six mirror planes of the group are perpendicular to the *a* and *c* axes. This orientation is not consistent with the symmetry of the space group. Inspection of zero through seven level Weissenberg photographs with the crystal rotated on the *c* axis yields no evidence that the space group is other than $P6_3/mmc$, $P6_3mc$, or $P\bar{6}2c$. It is our experience that the ordering of even so small a part of the structure as the sulfate oxygens would produce symmetry reduction that would be easily noticeable on photographs. Thus it must be concluded that the sulfate group is actually oriented with equal or nearly equal probability in three different ways, with its mirror plane normal to the a_1, a_2, and a_3 directions of the cell. This implies that the forces exerted on one sulfate group by adjacent sulfate groups are either insufficient to influence its orientation or that they are sufficient to be influential, and the resulting partly ordered pattern of orientations, in total, obeys the $\bar{6}$ symmetry of the space group; for example, the sulfate might rotate 120° for each *c* periodicity along the channel. A partly ordered arrangement would presumably produce unit cell changes; for example, a tripling of the *c* periodicity. No such changes were detectable on films. Sulfates in adjacent channels are separated by 10.2 Å, and those in the same channel by the *c* periodicity (9.1 Å).

Substitutional disorder appears to be superimposed on the positional disorder at the sulfate site with the substitution of $(NO_3)^-$ for $(SO_4)^{2-}$. The substitution is probably a one for one substitution since there is no evidence of $(NO_3)^-$ elsewhere in the structure. Admittedly, the nitrate is of low scattering power and at about 20 percent substitution it might be missed, particularly if disordered. The apparent one for one substitution relates to two immediate problems, the first of which is that of charge balance.

The assumption that charges must be balanced is usually made for chemical compounds and, when substitution occurs, leads to the formulation of sometimes elaborate charge compensation mechanisms. In the present case the substitution of $(NO_3)^-$ for $(SO_4)^{2-}$ is apparently compensated by omission of Cu^{2+} from Cu(5) site which would otherwise be half filled. Such a mechanism seems to require an interaction between the sulfate and Cu(5), which are separated by about 9.4 Å. Since this distance is comparable to the previously mentioned sulfate-sulfate distances and because both interactions are of Coulombic character, a very tenuous argument can be made that if charge balance is required in chemical compounds, the sulfates will take on a partly ordered pattern of orientations rather than being randomly oriented. If significant Coulombic interactions at distances of about 9 Å are not permissible, doubt is cast on the requirement for charge balance.

The second problem involved with the one for one substitution of $(NO_3)^-$ for $(SO_4)^{2-}$ is the question of ionic substitution between connellite and buttgenbachite. The apparent one for one substitution seems to imply that either the formula of buttgenbachite is incorrect, since it contains two nitrates for each sulfate in connellite, or there is not a smooth series between the two minerals. A second nitrate site would have to be developed somewhere in the series.

The large channel in connellite provides ample space for additional atoms and a second nitrate group could be accommodated with little distortion and no disorder. Presumably such an accommodation would place two nitrate groups across the mirror normal to *c* upon which the sulfate lies in connellite. This would tend to produce a lengthening and narrowing of the channel and this is the kind of distortion which is noted on comparison of connellite and buttgenbachite cell dimensions (Palache *et al.*, 1951).

The trigonal symmetry of the ring-like arrangement of the Cu–O polyhedra outlining the large channels passing through the connellite structure brings to mind homologous silicate structures such as beryl and some of the six-membered ring zeolites, *e.g.*, the chabazite group. The channelway in connellite has an aperture diameter of about 3.1 Å, assuming that O(12) is water and not structurally required. The aperture is larger than the opening in natrolite (2.6 Å, Bragg *et al.*, 1965), and is perhaps large enough to allow the passage of the sulfate and nitrate groups as well as water molecules. Symmetrical passage of the sulfate group through the constricted part of the channel would produce a closest approach of about 2.64 Å between a sulfate oxygen and the O(7) position of the framework. Substitution of Cl into the 0(7) site would make a tight fit, but thermal motion may make the dynamic aperture somewhat larger than its static dimensions (Bragg *et al.*, 1965). The sulfate ion is apparently held within the channel only by hydrogen bonding, since the sulfate oxygen to framework hydroxyl distances are 2.91 and 2.97 Å, and the sulfate oxygens are far from any Cu ion so that ionic interaction between $(SO_4)^{2-}$ and Cu^{2+} must be very weak. No ion exchange data are available to support the possibility that mutual substitution of sulfate-nitrate in the connellite-buttgenbachite series is of the zeolitic type, and the one for one nature of the substitution argues against such a possibility in the connellite part of the series *if* charge balance is required.

ACKNOWLEDGEMENTS

We are grateful to the Owens-Illinois Technical Center, Toledo, Ohio, for partial support in this work, and to the University of Arizona Computer Center for computer time.

REFERENCES

BRAGG, L., G. F. CLARINGBULL, AND W. H. TAYLOR (1965) *Crystal Structures of Minerals.* Cornell University Press, Ithaca, New York, 409p.

DANA, J. D. (1850) *System of Mineralogy,* 3rd ed., John Wiley and Sons, Inc., New York.

DONNAY, J. D. H., G. DONNAY, E. G. COX, O. KENNARD, AND M. V. KING (1963) Crystal Data. *Amer. Crystallogr. Assoc. Monogr.* **5**, 1302p.

FORD, W. E., AND W. M. BRADLEY (1915) On the identity of footeite with connellite together with the descriptions of two new occurrences of the mineral. *Amer. J. Sci.* **39**, 670–676.

HAMILTON, W. C. (1965) Significance tests on the crystallographic *R* factor. *Acta Crystallogr.* **18**, 502–510.

PALACHE, C., H. BERMAN, AND C. FRONDEL (1951) *The System of Mineralogy . . . of Dana Vol.* **2**, 7th ed. John Wiley and Sons, Inc., New York, 1124p.

SCHOEP, A. (1925) Sur la buttgenbachite, nouveau minéral. *C. R. Acad. Sci. Paris.* **181**, 421–423.

Manuscript received, September 13, 1971; accepted for publication, October 27, 1971.