Connellite
from
Bisbee, Arizona:
a Single-Crystal X-ray Study

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INTRODUCTION

We have reported single-crystal X-ray structures of three specimens of buttgenbachite, *ca.* $Cu_{36}Cl_6(NO_3)_2(OH)_{64} \cdot nH_2O$, from the Toughnut mine, Tombstone, Arizona, USA; the Likasi mine, Jadotville, Shaba Province, Democratic Republic of Congo; and the Cole shaft, Bisbee, Arizona (Hibbs *et al*., 2002, 2003a), together with the structure of a specimen of connellite from the Great Australia mine, Cloncurry, Queensland, Australia (Hibbs *et al*., 2003b). The nature of the connellite-buttgenbachite solid solution, with connellite being the sulfate-dominant, rather than nitrate-dominant end-member, is complex and the above studies have resolved certain structural difficulties associated with the oxyanions sites in the lattice (Fanfani *et al*., 1973; McLean and Anthony, 1972). Variability in stoichiometry arises from changes in occupancy of H_2O, H_3O^+ and Cl^- at the origin of the unit cell, of Cl^- and NO_3^- at two other sites in the lattice, and the substitution of sulfate for nitrate at one of the latter sites (Table 1). Variable amounts of "zeolitic" water in structural channels that contain sulfate and nitrate ions serve to further complicate the issue. Connellite is known from a number of mines in Arizona, particularly from around Bisbee (McLean and Anthony, 1972; Anthony *et al*., 1995). It would have been unlikely that all of the Bisbee material was buttgenbachite and a new single-crystal structure determination of a specimen from Bisbee, presented below, shows that it is connellite, albeit with some nitrate in the lattice.

Members of the series are difficult to distinguish from each other, but it is now certain that both connellite and buttgenbachite occur in the Bisbee deposits.
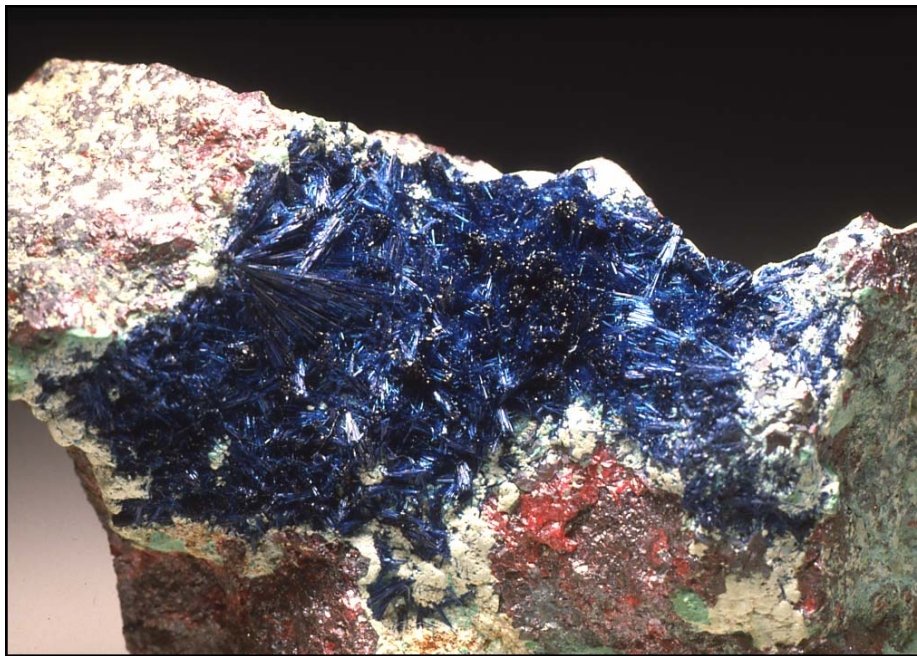

Figure 1. Connellite specimen, 8 cm across, from the Czar mine, Bisbee, Arizona. Harvard Mineralogical Museum collection; photo by Wendell E. Wilson.

EXPERIMENTAL

The crystal used for the structure determination was from the collection of the Arizona Sonora Desert Museum, Tucson, Arizona (specimen number ASDM 2031). Their specimen is from the Shattuck mine, Bisbee, Arizona, and that it was added to the collection in an early acquisition (Anna Dimitrovic, pers. comm., 2005). A crystal of dimensions 0.2 x 0.3 x 0.4 mm was mounted on an Enraf Nonius CAD4 diffractometer. Unit cell dimensions were determined by least-squares refinement of the setting angles for 25 reflections within the range $3.73 < \theta < 23.23^{\circ}$ and are listed in Table 1 together with associated crystal data. All data were collected at 293(2)K using graphite-monochromatized Mo Kα radiation, corrected for Lorentz and polarization effects and an empirical absorption correction based on phi scans was applied (Walker and Stuart, 1983). The structure was determined by difference Fourier techniques and refined on F^2 by full-matrix least-squares methods (Sheldrick, 1997) using all unique data. Scattering factors used were those given by Sheldrick (1997). A summary of crystal data and refinement details is given in Table 2.

A starting set of coordinates for copper, chloride and hydroxide ions, which form the Cu(II) polyhedral lattice of all the buttgenbachite-connellite type structures (Hibbs *et al*., 2003a, 2003b), including a partially occupied (~50%) chloride ion at the origin, refined smoothly with anisotropic displacement parameters to an R_1 of 0.065. A difference-Fourier map then revealed the positions of atoms in the large channel parallel to *c* and centred along (2/3, 1/3, *z*). As for the Great Australia mine connellite (Hibbs *et*

al., 2003b), the nitrogen, N(1), and oxygen, O(1), atoms of a reduced occupancy (~25%) nitrate ion centered at $z = 1/4$ and sharing the site with a reduced occupancy (~40%) chloride ion, Cl(4), were found. Further inspection of the difference Fourier map again revealed a small but significant peak ~0.5Å from N(1) along the c axis, which was positioned approximately tetrahedrally at a distance of ~1.5Å to each of the three oxygen atoms of the N(1),O(1) nitrate ion. This is the sulfur atom, S(1), of a sulfate ion of significant occupancy (~17%) with three of its oxygen atoms almost coincidental with the three oxygen atoms of the N(1),O(1) nitrate ion. Accordingly, O(1) could be split into O(1a), which was constrained to be 1.20 ± 0.01Å from N(1), and O(1b), which was constrained to be 1.48 ± 0.01Å from S(1) and which gave a nearly tetrahedral setting. The existence of this sulfate ion was confirmed with the subsequent location of the fourth oxygen atom, O(1c), ~1.5Å from S(1) along the c axis, and during subsequent refinement this oxygen atom also was constrained to be 1.48Å from S(1). A subsequent difference-Fourier map failed to reveal any further large channel contents centred at 2/3,1/3, z. However, a water molecule, OW, was found to partially occupy a site in the $z = 3/4$ region (at ~0.5, ~0.25, 3/4).

A final refinement was then performed via a sequence of steps in which the occupancies of all the atoms constituting the large channel contents and also the occupancy of the chloride ion, Cl(3), at the origin were refined, resulting in acceptable and similar isotropic thermal parameters for all atoms concerned. Final R_1 and wR_2 values were 0.046 and 0.151, respectively, for 522 reflections with $I > 2\sigma(I)$. Hydrogen atoms of the hydroxide ions or water molecules were not located in the structure. However, for the requirement of charge balance, a small proportion of the assigned hydroxide ions must be protonated. Final atomic coordinates, site occupancy factors and equivalent isotropic thermal parameters are listed in Table 3.

RESULTS AND DISCUSSION

The structure of the connellite determined in the present study is essentially the same as that described previously (Hibbs *et al.*, 2003b), where the Cu(II) polyhedral lattice formed by Cu(1), Cu(2), Cu(3), Cu(4), Cl(1), OH(1), OH(2), OH(3) and OH(4) as found for other members of the group (Hibbs *et al.*, 2003a) is again preserved The contents of the large "open" channels parallel to c wherein the NO_3^-, Cl^-, and SO_4^{2-} ions and H_2O molecules reside, are quite similar, but the sulfate ion content of this particular sample is significantly larger than that of nitrate ion; an empirical formula of $Cu_{36}Cl_{7.86}(SO_4)_{0.67}(NO_3)_{0.50}(OH)_{62.3} \cdot 5.6H_2O$ is found. As before, the nitrate ion is centered on a mirror at (2/3, 1/3,1/4) and shares the site with a chloride ion, the occupancy for which (41%) is slightly greater than that found in the Great Australia mine sample (36%). Again, the present structure shows no further occupation along the z axis at the center of the large channels, but the "constriction" point, once per c periodicity in these large channels, as defined by water molecules bonded to one of the copper ions, is worthy of comment. In the present structure these lattice water molecules occupy a 6-fold site (at x~0.50, y~0.25, z = 3/4) with an occupancy of 16%, and this is similar to the case found in the Likasi sulfate-bearing buttgenbachite and various other buttgenbachite crystals (Hibbs *et al.*, 2003a); these had population parameters ranging from 17% to 25%. However, in the Great Australia connellite (Hibbs *et al.*, 2003b) and in the Bisbee

buttgenbachite structure (Hibbs *et al.*, 2002) the lattice water molecules are located at a 12-fold site (but similarly positioned at x~0.50, y~0.25, z~0.80) with population parameters of 15% and 20%, respectively.

Finally, the origin site in the narrow channels running parallel to the *c* axis and centered around (0,0,z) is again considered to be occupied by a chloride ion, Cl(3), and with a population parameter of 52% this is similar to the 55% occupancy found in the Great Australia connellite (Hibbs *et al.*, 2003b) and to the 60% occupancy found in the Likasi sulfate-bearing buttgenbachite (Hibbs *et al.*, 2003a). A comparison of the contents of the large and small channels in the various connellite-buttgenbachite-type structures reported so far is shown in Table 1. Given the complex nature of solid solution in the connellite-buttgenbachite series, definite end-member compositions are impossible to define. Previously (Hibbs *et al.*, 2003b), we have adopted the simple expedient of naming connellite as that phase with mol% SO_4^{2-} > mol% NO_3^-. In this case, the material we have presently examined from Bisbee is clearly connellite.

SUPPLEMENTARY MATERIAL

Full lists of crystallographic data excluding structure factor tables have been deposited with the Inorganic Crystal Structure Database (ICSD), Fachinformationszentrum, Karlsruhe, Germany; CRYSDATA@FIZ-Karlsruhe.DE. Any request to the ICSD for this material should quote the full literature citation and the CSD-number 415129 (filename BisbeeConnCif). Lists of observed and calculated structure factors are available from the authors upon request.

ACKNOWLEDGEMENTS

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Table 1. **Comparison of the contents of the large and small channels in various connellite-buttgenbachite-type structures, with the % occupancies of the sites shown in parentheses.**

	1	2	3	4	5	6
(a) Large channels centred along (2/3, 1/3, z)						
Site #1	Cl⁻	Cl⁻	Cl⁻	Cl⁻	Cl⁻	Cl⁻
$z = 1/4$	(25%)	(45%)	(30%)	(50%)	(36%)	(41%)
		NO_3^-	NO_3^-	NO_3^-	NO_3^-	NO_3^-
		(55%)	(18%)	(50%)	(24%)	(25%)
$z \sim 0.20$			SO_4^{2-}		SO_4^{2-}	SO_4^{2-}
and ~ 0.30			(9%)		(13%)	(17%)
Site #2	NO_3^-		NO_3^-			
$z \sim 0.08$	(37.5%)		(24%)			
and ~ 0.42			H_2O			
			(6%)			
Lattice H_2O						
at ~ 0.50, ~ 0.25, 3/4	(25%)	(17%)	(18%)			(16%)
at ~ 0.50, ~ 0.25, ~ 0.80				(20%)	(15%)	
(b) Small channels centred along (0, 0, z)						
Origin	H_3O^+	Cl⁻	Cl⁻	Cl⁻	Cl⁻	Cl⁻
$z = 0, 1/2$	(100%)	(50%)	(60%)	(55%)	(55%)	(52%)

1. Likasi mine, Jadotville, Shaba Province, Democratic Republic of Congo (Fanfani *et al*., 1973; Hibbs *et al*., 2003a).
2. Toughnut mine, Tombstone, Arizona (McLean and Anthony, 1973; Hibbs *et al*., 2003a).
3. Likasi mine, Jadotville, Shaba Province, Democratic Republic of Congo (Hibbs *et al*., 2003a).
4. Cole shaft, Bisbee (Hibbs *et al*., 2002).
5. Great Australia mine, Cloncurry, Queensland, Australia (Hibbs *et al*., 2003b).
6. Shattuck mine, Bisbee (this work).

Table 2. Crystal data and structure refinement details for Bisbee connellite.

Empirical formula	$H_{73.50}Cl_{7.86}Cu_{36}N_{0.50}O_{72.08}S_{0.67}$
Formula weight	3821.93
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	$P6_3/mmc$
Unit cell dimensions	a = 15.7866(15) Å
	c = 9.1015(12) Å
Volume	1964.4(4) Å^3
Z	1
Density (calculated)	3.231 g cm^{-3}
Absorption coefficient	9.905 mm^{-1}
$F(000)$	1842
Crystal size	0.4 x 0.3 x 0.2 mm
θ range for data collection	3.73 to 23.23°
Index ranges	$-8 \le h \le 0, 0 \le k \le 17, 0 \le l \le 10$
Reflections collected	522
Independent reflections	522 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	522/2/63
Goodness-of-fit on F^2	1.144
Final R indices [$I>2\sigma(I)$]*	R_1 = 0.0463, R_w = 0.1510
R indices (all data)	R_1 = 0.0478, R_w = 0.1525
Extinction coefficient	0.0007(4)

*The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.0938P)^2 + 31.6P]$ where $P = [Max(F_o)^2 + 2(F_c)^2]/3$ as defined by SHELX-97 (Sheldrick, 1997).

Table 3. **Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) and site occupancy factors (sof) for Bisbee connellite.** 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	14(1)	0.25
Cu(2)	2011(1)	0	0	12(1)	0.5
Cu(3)	3364(2)	1682(1)	7500	10(1)	0.25
Cu(4)	3585(1)	165(1)	2500	10(1)	0.5
Cl(3)	0	0	0	11(3)	0.043
Cl(1)	2772(3)	1386(2)	2500	12(1)	0.25
OH1	4504(4)	3707(4)	918(6)	12(1)	1.0
OH2	749(3)	-749(3)	989(9)	20(2)	0.5
OH3	6744(4)	7442(4)	1102(6)	11(1)	1.0
OH4	4424(4)	5576(4)	2500	14(3)	0.25
OW	5070(60)	2540(30)	7500	17(16)	0.040
Cl(4)	6667	3333	2500	15(6)	0.034
N(1)	6667	3333	2500	15(6)	0.021
O(1a)	6226(4)	3774(4)	2500	17(5)	0.063
O(1b)	6150(7)	3850(7)	2500	17(5)	0.084
S(1)	6667	3333	2999(54)	14(8)	0.028
O(1c)	6667	3333	4620	14(8)	0.028