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Hoganite and paceite, two new acetate minerals from the Potosi mine, Broken Hill, Australia

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ABSTRACT

Hoganite, copper(II) acetate monohydrate, and paceite (pronounced 'pace-ite'), calcium(II) copper(II) tetraacetate hexahydrate, occur as isolated crystals embedded in ferruginous gossan from the Potosi Pit, Broken Hill, New South Wales, Australia. They are associated with goethite, hematite, quartz, linarite, malachite, azurite, cerussite and cuprian smithsonite. Hoganite is bluish green with a pale blue streak and a Mohs hardness of 1½; it possesses perfect {001} and distinct {110} cleavages and has a conchoidal fracture. Chemical analysis of hoganite gave (wt.%) C 23.85; H 3.95; Cu 31.6; Fe 0.4; O (by difference) 40.2, yielding an empirical formula of $C_4H_{7.89}O_{5.07}Cu_{1.00}Fe_{0.01}$. The simplified formula is $C_4H_8O_5Cu$ or $Cu(CH_3COO)_2.H_2O$, the mineral being identical to the synthetic compound of the same formula. Single-crystal X-ray data for hoganite are: monoclinic, space group $C2/c$, $a = 13.162(3)$, $b = 8.555(2)$, $c = 13.850(3)$ Å, $\beta = 117.08(3)°$, $Z = 8$. The density, calculated from single-crystal data, is 1.910 g cm^{-3}. The strongest lines in the X-ray powder pattern are [d_{obs} (I_{obs}) (hkl)] 6.921 (100) (011); 3.532 (28) (202); 6.176 (14) (200); 3.592 (11) ($\bar{1}22$); 5.382 (10) ($\bar{2}11$); 2.278 (10) (204); 5.872 (9) (002). Hoganite (orientation presently unknown) is biaxial positive with $\alpha = 1.533(2)$, $\beta = 1.541(3)$, $\gamma = 1.554(2)$, 2V(meas.) = 85(5)°, 2V(calc.) = 76.8°, dispersion is $r < v$, medium (white light); it is strongly pleochroic with X = blue, Y = pale bluish, Z = pale bluish green and absorption $X > Y > Z$. The mineral is named after Graham P. Hogan of Broken Hill, New South Wales, Australia, a miner and well-known collector of Broken Hill minerals.

Paceite is dark blue with a pale blue streak and a Mohs hardness of 1½; it possesses perfect {100} and {110} cleavages and has an uneven fracture. Chemical analysis of paceite gave (wt.%) C 21.25; H 5.3; Ca 9.0; Cu 14.1; O (by difference) 50.35, yielding an empirical formula of $C_8H_{23.77}O_{14.23}Ca_{1.02}Cu_{1.00}$. The simplified formula is $C_8H_{24}O_{14}CaCu$ or $CaCu(CH_3COO)_4.6H_2O$, the mineral being identical to the synthetic compound of the same formula. Unit-cell data (refined from X-ray powder diffraction data) for paceite are: tetragonal, space group $I4/m$, $a = 11.155(4)$, $c = 16.236(17)$ Å, $Z = 4$. The density, calculated from refined cell data, is 1.472 g cm^{-3}. The strongest lines in the X-ray powder pattern are [d_{obs} (I_{obs}) (hkl)] 7.896 (100) (110); 3.530 (20) (310); 5.586 (15) (200); 8.132 (8) (002); 9.297 (6) (101); 2.497 (4) (420); 3.042 (3) (321). Paceite is uniaxial positive with $\omega = 1.439(2)$ and $\varepsilon = 1.482(3)$ (white light); pleochroism is bluish with a greenish tint (O), pale bluish with a greyish tint (E), and absorption $O \geqslant E$. The mineral is named after Frank L. Pace of Broken Hill, New South Wales, Australia, an ex-miner and well-known collector of Broken Hill minerals.

KEYWORDS: hoganite, paceite, new mineral, acetate, Broken Hill, Australia.

Introduction

THE Potosi Ag-Pb-Zn deposit lies some 2 km northeast of Broken Hill, New South Wales, Australia, at 31°56′S 141°30′E. It is of the same

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style of mineralization as the giant Broken Hill deposits and was recently open cut by Pasminco-Broken Hill Limited, starting in 1996 (Mortland and Webster, 1998). Intermittent, small-scale mining of the deposit was begun before 1894 by the Potosi Silver Mining Company, which sank a shaft to a depth of 60 m. The Broken Hill Proprietary Company took over the leases in 1909 and sank a new shaft to the same depth (Andrews, 1922; Jaquet, 1894); sporadic mining continued until 1927, during which time ~3000 tonnes of ore were extracted. The oxidized zone mineralogy is similar to that of the main Broken Hill lode (Birch, 1999) and was exposed during recent mining operations. Gossan recovered at a depth of ~20 m near the old main shaft was in the vicinity of a mass of decomposing leaf litter and carried goethite, hematite, quartz, linarite, malachite, azurite, cuprian smithsonite and cerussite. Close examination of the material revealed the presence of two new acetate minerals, $Cu(CH_3COO)_2.H_2O$ (hoganite) and $CaCu(CH_3COO)_4.6H_2O$ (paceite), associated with some of these phases.

Hoganite is named in honour of Mr Graham P. Hogan (1957−) of Broken Hill, New South Wales, Australia, a miner and well-known collector of Broken Hill minerals, who originally recovered the material. He also provided the locality information and observations about the association of the minerals with decomposing vegetable matter. The mineral and name were approved by the IMA Commission on New Minerals and Mineral Names in 2001 (2001-029). Paceite is named in honour of Mr Frank L. Pace (1948−) of Broken Hill, New South Wales, Australia, an ex-miner and well-known collector of Broken Hill minerals, who drew the new minerals to our attention. The mineral and name were approved by the IMA Commission on New Minerals and Mineral Names in 2001 (2001-030). Type material for both phases is deposited in the Museum of Victoria, Melbourne (M47465), and co-type material in the Australian Museum, Sydney, and the Broken Hill Geocentre, Broken Hill.

Hoganite

Hoganite was found as isolated, bluish green prisms up to 0.6 mm long in ferruginous gossan. Because of the very few crystals of this mineral in the original specimens, and because they seemed quite different to any known species, it was decided to proceed directly to a single-crystal X-ray structure analysis. A single crystal of dimensions 0.35 × 0.25 × 0.20 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 $2.95 < \theta < 26.29°$. This resulted in the following crystal data: $C_4H_8O_5Cu$, M_r = 199.64, monoclinic, space group $C2/c$, a = 13.162(3) Å, b = 8.555(2) Å, c = 13.850(3) Å, β = 117.08(3)°, V = 1388.6(5) Å^3, Z = 8, D_c = 1.910 g cm^{-3}, μ(Mo-$K\alpha$) = 3.107 mm^{-1}, $F(000)$ = 808.

Intensity data were collected at 293 K using graphite-monochromatized Mo-$K\alpha$ radiation and these were corrected for Lorentz and polarization effects; an empirical absorption correction based on phi scans was applied. The structure was solved by direct methods (SHELX-90; Sheldrick, 1990) and difference Fourier techniques and refined on F^2 by full-matrix least-squares methods (SHELXL-97; Sheldrick, 1997) using all unique data and scattering factors for neutral atoms. At this stage, it was obvious that the mineral was the well-known compound copper(II) acetate monohydrate. A refinement with an empirical extinction correction applied (anisotropic for non-hydrogen atoms with hydrogen atoms riding on the atoms to which they are attached) for 1413 independent reflections ($I > 2\sigma(I)$) converged to R = 0.062 and $wR2$ = 0.191, with $w = 1/(\sigma^2(F_o)^2 + (0.136P)^2 + 6.26P)$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$, as defined by SHELXL-97. Because the structure is in excellent agreement with previously reported determinations (de Meester *et al.*, 1973; Langs and Hare, 1967), the details are not repeated here. However, full lists of crystallographic data concerning the single-crystal structure determination for hoganite have been deposited with the Editor and are available upon request and are included in the online version of the paper (www.minersoc.org).

Powder X-ray diffraction data were collected on natural material using a Philips PW1925-10 powder diffractometer (Cu-$K\alpha$ X-radiation, λ = 1.5418 Å) with pure Si as internal standard. Unit-cell parameters refined from powder data were a = 13.845(21), b = 8.528(24), c = 13.197(21) Å, β = 117.1(1)°, V = 1387.1(12) Å^3, Z = 8 (note that the cell constants are quoted here for the alternative space group setting of $A2/a$, so that the powder data are directly comparable to those listed in the PDF data file 27-145). Recorded data show good agreement with the cell of de Meester *et al.*

(1973) for space group setting *C*2/*c* and with data reported on PDF card 27-145 (Table 1).

Qualitative energy-dispersive X-ray analyses (EDS) of hoganite using a scanning electron microscope yielded only Cu. Wet-chemical analyses of Ca, Cu, Mg, Zn, Pb and Fe on handpicked natural material were carried out by AAS. Carbon and hydrogen were determined with

TABLE 1. Powder X-ray diffraction data for hoganite.

This work				PDF card 27-145 for $Cu(CH_3COO)_2.H_2O$	
I(rel.)	*d*(meas.)	*d*(calc.)	*hkl**	*I*(rel.)	*d*(meas.)
100	6.921	6.901	011	100	6.91
14	6.176	6.162	200	35	6.17
9	5.872	5.874	002	25	5.87
7	5.747	5.760	$\bar{2}02$	16	5.75
10	5.382	5.365	$\bar{2}11$	25	5.38
			020	2	4.28
			211	4	4.09
			$\bar{3}11$	2	4.05
11	3.592	3.581	$\bar{1}22$	12	3.588
28	3.532	3.525	202	20	3.527
			$\bar{4}02$	4	3.455
6	3.429	3.427	$\bar{2}22$	4	3.434
			$\bar{2}04$	4	3.292
4	3.087	3.081	400	4	3.087
			$\bar{4}13$	2	3.033
4	2.925	2.958	$\bar{3}20$	2	2.967
			$\bar{4}04$	2	2.875
			031	2	2.773
			222	2	2.723
			$\bar{4}22$	2	2.688
			131	2	2.645
			$\bar{2}24$	2	2.609
			$\bar{5}13$	2	2.592
			411	<1	2.576
7	2.546	2.543	$\bar{3}24$	4	2.543
6	2.513	2.513	$\bar{2}15$	2	2.510
			$\bar{3}15$	2	2.495
			$\bar{3}31$	2	2.425
			$\bar{4}15$	4	2.393
4	2.387	2.386	$\bar{4}24$	4	2.387
4	2.332	2.327	402	8	2.330
9	2.291	2.285	$\bar{3}33$	10	2.290
10	2.278	2.279	204	4	2.279
5	2.227	2.225	$\bar{6}04$	4	2.226
			124	4	2.222
			$\bar{5}24$	2	2.186
			511	1	2.149
5	2.128	2.131	$\bar{6}11$	2	2.137
			$\bar{1}42$	2	2.035
			$\bar{6}15$	4	2.027
			$\bar{6}24$	1	1.976
			413	4	1.963
4	1.951	1.954	$\bar{3}26$	2	1.952
			Plus 30 extra lines to 1.373		

* With respect to alternative setting of cell in space group *A*2/*a* of PDF card 27-145.

an elemental analyser. H_2O and CO_2 were the materials analysed after combustion; insufficient material was available for separate water analysis. The results obtained (wt.%) were C, 23.8, 23.9, av. 23.85; H, 3.9, 4.0, av. 3.95; Cu, 31.5, 31.7, av. 31.6; Fe, 0.4, 0.4, av. 0.4; O (by difference), 40.2, corresponding to an empirical formula of $C_4H_{7.89}O_{5.07}Cu_{1.00}Fe_{0.01}$ based on 4 carbons in the formula unit and ideally $C_4H_8O_5Cu$; calculated for $C_4H_8O_5Cu$: C, 24.06; H, 4.04; Cu, 31.83; O, 40.07%. A trace of Zn is present but no Pb, Mg or Ca was detected. The small amount of Fe present may be due to gossan particles adhering to the hand-picked sample.

Hoganite is transparent, dark bluish green with a pale blue streak and a vitreous lustre. It does not fluoresce under UV light. Its Mohs hardness is 1½. Cleavage was not determined on natural material because of insufficient quantity. Winchell (1954) reported perfect {001} and

TABLE 2. Powder X-ray diffraction data for paceite.

This work				PDF card 32-159 for $CaCu(CH_3COO)_4.6H_2O$	
I(rel.)	*d*(meas.)	*d*(calc.)	*hkl*	*I*(rel.)	*d*(meas.)
6	9.297	9.194	101	1	9.20
8	8.132	8.117	002	12	8.11
100	7.896	7.888	110	100	7.89
15	5.586	5.576	200	30	5.58
1	4.770	4.769	211	2	4.770
			202	1	4.600
			004	1	4.060
2	3.675	3.668	213	12	3.670
2	3.616	3.609	114	11	3.611
20	3.530	3.527	310	35	3.528
			204	4	3.284
			312	1	3.236
3	3.042	3.039	321	6	3.040
1	2.831	2.828	224	3	2.831
1	2.689	2.686	323	11	2.687
1	2.667	2.669	411	1	2.670
2	2.632	2.629	330	2	2.628
			116	1	2.561
4	2.497	2.494	420	4	2.495
			305	1	2.447
			404	2	2.299
			431	1	2.210
2	2.190	2.188	510	3	2.188
1	2.128	2.125	424	6	2.126
1	2.064	2.063	433	1	2.066
1	2.027	2.029	008	4	2.031
1	1.973	1.972	440	1	1.972
1	1.969	1.968	307	1	1.969
1	1.928	1.926	514	3	1.926
2	1.916	1.913	530	5	1.913
1	1.861	1.859	600	2	1.859
			444	1	1.774
1	1.762	1.764	620	3	1.764
			318	3	1.760
1	1.732	1.737	613	2	1.737
1	1.727	1.732	541	1	1.732
			624	1	1.618
			550	1	1.577
1	1.549	1.547	640	1	1.547

distinct $\{110\}$ cleavages on synthetic crystals. No parting was observed. Tenacity is brittle and fracture, conchoidal. Thermal behaviour and solubility data (soluble in water) for synthetic hoganite are given in Gmelin (1961*a*). In natural material, hoganite is present as short, prismatic, thick tabular crystals. Forms observed are similar to those of synthetic crystals, for which Bell *et al.* (1995) reported $\{10\bar{1}\}$ (tabular form), $\{01\bar{1}\}$, $\{2\bar{1}\bar{1}\}$, $\{110\}$ and $\{1\bar{1}\bar{2}\}$. Winchell (1954) reported crystal $\{110\}$ tablets with $\{001\}$, $\{100\}$, $\{20\bar{1}\}$. No twinning was observed in natural material but some synthetic crystals show butterfly-like twins.

Due to the very small amount of the natural material, optical properties were determined on synthetic crystals grown from aqueous solution, measured in white light. Hoganite is biaxial positive, $\alpha = 1.533(2)$, $\beta = 1.541(3)$, $\gamma = 1.554(2)$, 2V(meas.) = 85(5)°, 2V(calc.) = 76.8°, dispersion $r < v$ (medium), orientation presently unknown. It is strongly pleochroic with X = blue, Y = pale bluish, Z = pale bluish green; absorption $X > Y > Z$. Winchell (1954) did not give data for $Cu(CH_3COO)_2.H_2O$, but reported indices, 2V and pleochroism for "verdigris or basic copper acetate", which is now known to be identical to $Cu(CH_3COO)_2.H_2O$ (Dunn, 1981). These data show good agreement with the optical properties determined in this study. The Gladstone-Dale compatibility, $1\text{-}(K_P/K_C)$, calculated for the ideal formula is 0.010 (superior).

Paceite

On some of the hoganite-bearing specimens were dark blue, short, prismatic, tetragonal crystals up to 1 mm across and thin crusts of intergrown microcrystals. A single-crystal structure analysis was not attempted, but powder X-ray diffraction studies and chemical analyses established that the mineral was identical to the known synthetic compound calcium copper acetate hexahydrate, $CaCu(CH_3COO)_4.6H_2O$, for which the crystal structure is well known (Langs and Hare, 1967; Klop *et al.*, 1983). Powder X-ray diffraction data were collected as above (Table 2) and showed excellent agreement with data reported on PDF card 32-159. Refined cell constants from the powder data gave a = 11.155(4), c = 16.236(17) Å, V = 2020.3(21) Å^3, tetragonal, space group $I4/m$, with D(calc.) = 1.472 g cm^{-3}, Z = 4. Unit-cell data show good agreement with those published previously (Table 3).

Qualitative SEM (EDS) studies of paceite detected only Ca and Cu. Analyses of a hand-picked sample of natural material were carried out as for hoganite (AAS for Ca). C and H were determined with an elemental analyser. H_2O and CO_2 were the materials analysed after combustion; insufficient material was available for separate water analysis. Results obtained (wt.%) were C 21.2, 21.3, av. 21.25; H 5.3.5.3, av. 5.3; Cu 14.0, 14.2, av. 14.1; Ca 8.9, 9.1, av. 9.0; O (by difference) 50.35, corresponding to an empirical formula of $C_8H_{23.77}O_{14.23}Ca_{1.02}Cu_{1.00}$ based on 8 carbons in the formula unit and ideally $C_8H_{24}O_{14}CaCu$; calculated for $C_8H_{24}O_{14}CaCu$: C 21.45; H 5.40; Cu 14.19; Ca 8.95; O 50.01%. Traces of Pb and Zn were found but no Mg or Fe was detected.

Paceite is translucent, deep sky blue with a pale blue streak, vitreous lustre, a Mohs hardness of 1½, an uneven fracture and a brittle tenacity. Cleavage is perfect on $\{100\}$ and $\{110\}$; no parting was observed. The mineral does not fluoresce under UV light. Paceite is an incongruently-saturating double salt; recrystallization in the absence of excess Ca^{2+} gives rise to $Cu(CH_3COO)_2.H_2O$ (Gmelin, 1961*b*; Holden and Singer, 1961). The salt is readily soluble in water and data for dehydration of synthetic paceite are

TABLE 3. Unit-cell data for paceite (refined from X-ray powder data) and its synthetic analogue*.

	Paceite	$CaCu(OAc)_4.6H_2O$	$CaCu(OAc)_4.6H_2O$	$CaCu(OAc)_4.6H_2O$
Ref.	This work	Klop *et al.* (1983)	Langs and Hare (1967)	PDF card 32-159
Space group	$I4/m$ (by analogy)	$I4/m$	$I4/m$	$I4/m$
a (Å)	11.155(4)	11.152(2)	11.183	11.158
c (Å)	16.226(17)	16.240(1)	16.277	16.249
V (Å^3), Z	2020.13(21), 4	2019.7(5), 4	2035, 4	2023.0, 4

*OAc = acetate ion

given in Gmelin (1961*b*). Single crystals of natural material are short tetragonal prisms, sometimes with bevelled corners, displaying forms {100}, {001} and {111}; other forms reported by Winchell (1954) for synthetic material, {110}, were not observed. Twinning was not evident.

Due to the very small amount of the natural material, optical properties were determined on synthetic crystals grown from aqueous solutions following the method of Holden and Singer (1961).

Optical properties measured in white light showed good agreement with those given by Winchell (1954). Paceite is uniaxial positive with ω = 1.439(2), ε = 1.482(3). The mineral is pleochroic with O = bluish with a greenish tint and E = (pale) bluish with a greyish tint; absorption O $\geqslant$ E. The Gladstone-Dale compatibility, 1-(K_P/K_C), calculated for the ideal formula, is -0.020 (excellent).

Discussion

Acetate minerals are rare, despite the fact that acetic acid is common in the biosphere. Palache *et al.* (1951) mention only calclacite, calcium acetate chloride pentahydrate, as a product formed on calcareous fossils and pottery stored in oak cases. Supposedly natural acetates have been reported in the past (Dunn, 1981; Žáček, 1991). In particular, Dunn (1981) reported a specimen consisting of copper acetate hydrate on native copper from the Onganja mine, Southwest Africa, but it was suggested that the compound might not have been of natural origin. The minerals reported here are of natural origin, the acetate ion having been furnished in this case as a result of the decomposition of leaf litter and possibly mine timbers in the immediate vicinity of the recovered material. We note that these are the first naturally-occurring acetate minerals, given that calclacite is essentially a museum artefact.

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TABLE 1S. Crystal data and structure refinement for hoganite.

Empirical formula	$C_4H_8CuO_5$	
Formula weight	199.64	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$C2/c$	
Unit-cell dimensions	a = 13.162(3) Å	
	b = 8.555(2) Å	β = 117.08(3)°
	c = 13.850(3) Å	
V	1388.6(5) $Å^3$	
Z	8	
Density (calculated)	1.910 mg/m^3	
Absorption coefficient	3.107 mm^{-1}	
$F(000)$	808	
Crystal size	0.35 × 0.25 × 0.20 mm	
2θ range for data collection	2.97 to 26.29°	
Index ranges	$-16 \leqslant h \leqslant 16$, $-10 \leqslant k \leqslant 10$, $-9 \leqslant l \leqslant 17$	
Reflections collected	2888	
Independent reflections	1413 [R(int) = 0.0782]	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1413/U_{iso} of H atoms, C-H distances/102	
Goodness-of-fit on F^2	1.062	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0622, R_w = 0.1905	
R indices (all data)	R_1 = 0.0643, R_w = 0.1934	
Extinction coefficient	0.027(3)	

TABLE 2S. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for hoganite. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}
Cu(01)	4500(1)	840(1)	448(1)	20(1)
O(3)	3158(4)	882(4)	−1010(3)	28(1)
O(2)	6011(3)	607(5)	1768(3)	30(1)
O(4)	4048(3)	−1209(5)	744(3)	33(1)
O(1)	5080(3)	2643(4)	1(3)	33(1)
O(5)	3753(4)	2076(6)	1323(3)	39(1)
C(3)	3180(4)	205(6)	−1804(3)	24(1)
C(1)	4344(4)	−2480(7)	510(4)	26(1)
C(2)	6032(6)	3953(7)	-850(5)	39(1)
C(4)	2168(5)	360(9)	−2883(4)	45(2)

TABLE 3S. Selected bond lengths [Å] and angles [°] for hoganite.

Cu(01)–O(1)	1.944(4)	O(3)–Cu(01)–O(5)	98.12(17)
Cu(01)–O(4)	1.953(4)	O(2)–Cu(01)–O(5)	93.04(17)
Cu(01)–O(3)	1.988(4)	O(1)–Cu(01)–Cu(01)#1	85.93(13)
Cu(01)–O(2)	2.007(4)	O(4)–Cu(01)–Cu(01)#1	82.75(12)
Cu(01)–O(5)	2.154(4)	O(3)–Cu(01)–Cu(01)#1	86.21(12)
Cu(01)–Cu(01)#1	2.6134(12)	O(2)–Cu(01)–Cu(01)#1	82.72(12)
O(3)–C(3)	1.255(6)	O(5)–Cu(01)–Cu(01)#1	174.39(12)
O(2)–C(3)#1	1.253(6)	C(3)–O(3)–Cu(01)	121.2(3)
O(4)–C(1)	1.247(7)	C(3)#1–O(2)–Cu(01)	124.3(3)
O(1)–C(1)#1	1.259(7)	C(1)–O(4)–Cu(01)	124.6(4)
O(5)–HW1	0.75(8)	C(1)#1–O(1)–Cu(01)	121.0(4)
O(5)–HW2	0.85(9)	Cu(01)–O(5)–HW1	114(7)
C(3)–O(2)#1	1.253(6)	Cu(01)–O(5)–HW2	135(6)
C(3)–C(4)	1.488(7)	HW1–O(5)–HW2	109(9)
C(1)–O(1)#1	1.259(7)	O(3)–C(3)–O(2)#1	125.4(4)
C(1)–C(2)#1	1.506(7)	O(3)–C(3)–C(4)	118.1(4)
C(2)–C(1)#1	1.506(7)	O(2)#1–C(3)–C(4)	116.4(5)
C(2)–H(2A)	0.9600	O(4)–C(1)–O(1)#1	125.6(5)
C(2)–H(2B)	0.9600	O(4)–C(1)–C(2)#1	117.6(5)
C(2)–H(2C)	0.9600	O(1)#1–C(1)–C(2)#1	116.8(5)
C(4)–H(4A)	0.9600	C(1)#1–C(2)–H(2A)	109.5
C(4)–H(4B)	0.9600	C(1)#1–C(2)–H(2B)	109.5
C(4)–H(4C)	0.9600	H(2A)–C(2)–H(2B)	109.5
		C(1)#1–C(2)–H(2C)	109.5
O(1)–Cu(01)–O(4)	168.65(17)	H(2A)–C(2)–H(2C)	109.5
O(1)–Cu(01)–O(3)	87.59(15)	H(2B)–C(2)–H(2C)	109.5
O(4)–Cu(01)–O(3)	90.85(16)	C(3)–C(4)–H(4A)	109.5
O(1)–Cu(01)–O(2)	89.94(16)	C(3)–C(4)–H(4B)	109.5
O(4)–Cu(01)–O(2)	89.43(17)	H(4A)–C(4)–H(4B)	109.5
O(3)–Cu(01)–O(2)	168.80(17)	C(3)–C(4)–H(4C)	109.5
O(1)–Cu(01)–O(5)	97.78(17)	H(4A)–C(4)–H(4C)	109.5
O(4)–Cu(01)–O(5)	93.57(18)	H(4B)–C(4)–H(4C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 $-x+1,-y,-z$

TABLE 4S. Anisotropic displacement parameters (Å^2 × 10^3) for hoganite. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2\, a^{*2}U_{11} + ... + 2\, h\, k\, a^*\, b^*\, U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(01)	21(1)	23(1)	18(1)	0(1)	12(1)	1(1)
O(3)	32(2)	31(2)	26(2)	1(1)	18(2)	4(1)
O(2)	27(2)	37(2)	25(2)	3(2)	13(2)	7(2)
O(4)	36(2)	31(2)	40(2)	3(2)	25(2)	−3(2)
O(1)	41(2)	26(2)	39(2)	3(2)	24(2)	−3(2)
O(5)	54(2)	46(2)	34(2)	14(2)	34(2)	24(2)
C(3)	19(2)	31(3)	19(2)	4(2)	7(2)	1(2)
C(1)	22(2)	33(3)	22(2)	7(2)	7(2)	−3(2)
C(2)	42(3)	34(3)	41(3)	10(2)	18(3)	−11(2)
C(4)	34(3)	67(4)	23(2)	−3(3)	4(2)	12(3)

TABLE 5S. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters (Å^2 × 10 ^{3}) for hoganite.

	x/a	y/b	z/c	U_{iso}
HW1	3860(70)	1710(110)	1850(60)	60(20)
HW2	3270(70)	2810(110)	1180(70)	70(30)
H(2A)	5573	4814	−833	59
H(2B)	5945	3829	−1573	59
H(2C)	6819	4156	−362	59
H(4A)	2301	1177	−3287	67
H(4B)	1509	611	−2787	67
H(4C)	2042	−609	−3271	67