Description and crystal structure of nyholmite, a new mineral related to hureaulite, from Broken Hill, New South Wales, Australia

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ABSTRACT

Nyholmite, $Cd_3Zn_2(AsO_3OH)_2(AsO_4)_2 \cdot 4H_2O$, from the Block 14 Opencut, Broken Hill, New South Wales, Australia, is a new Cd-Zn arsenate species, isostructural with the minerals of the hureaulite group. The mineral occurs in a quartz-garnet-arsenopyrite matrix as white globules, tufted aggregates of fibrous crystals and radiating hemispheres of thin, colourless, bladed crystals. Associated minerals are goldquarryite, lavendulan-sampleite, scorodite-strengite and gypsum. Individual crystals are up to 0.2 mm in length and 0.05 mm across. The mineral is transparent to translucent with a vitreous lustre. It is brittle with an uneven fracture and a white streak. The Mohs hardness is 3−3.5 and the calculated density is 4.23 g cm^{-3} for the empirical formula. Electron microprobe analyses yielded CdO 34.58, ZnO 9.72, MnO 3.59, CuO 3.39, Al$_2$O$_3$ 0.20, CaO 0.16, PbO 0.37, As$_2$O$_5$ 34.55, P$_2$O$_5$ 6.29 totalling 92.85 wt.%. The empirical formula, based on 20 oxygen atoms, is Ca$_{0.03}$Pb$_{0.02}$ Cd$_{2.80}$Al$_{0.04}$Zn$_{1.24}$- Cu$_{0.44}$Mn$_{0.53}$[(AsO$_4$)$_{3.13}$(PO$_4$)$_{0.92}$]$_{\Sigma 4.05}$H$_{1.91}$·3.79H$_2$O. Nyholmite is monoclinic, $C2/c$, a = 18.062(4) Å, b = 9.341(2) Å, c = 9.844(2) Å, β = 96.17(3)°, V = 1651.2(6) Å^3 (single-crystal data, at 123 K). The six strongest lines in the X-ray powder diffraction pattern are [d(Å),I,(hkl)]: 8.985,30,(200); 8.283,85,(110); 6.169,25,(111); 4.878,25,(002); 3.234,100,($2\bar{2}\bar{2}$, 420); 3.079,65,(222, 511); 2.976,45,(113). The crystal structure was solved by Patterson methods and refined using 2045 observed reflections to $R1(F)$ = 3.73%. The structure is characterized by a kinked, five-membered chain of edge-sharing $M\phi_6$ (ϕ = unspecified anion) octahedra, or pentamer, that extends in the a direction. The pentamers link by sharing corners to form a sheet in the (001) plane. Pentamers are also linked, *via* corner-sharing, by (As,P)O$_4$ groups forming thick slabs in the (001) plane. The slabs link in the c direction by corner-sharing between octahedra and tetrahedra to form a dense heteropolyhedral framework. Moderate to weak hydrogen-bonding provides additional linkage between the slabs.

Introduction

CADMIUM is a widespread trace element in many Pb and Zn ores (e.g. Berry *et al.*, 1983). Typically, it is found as an isomorphic replacement (substitution for a particular metal within the crystal lattice) in sulphide minerals. Galena and especially sphalerite readily absorb Cd through isomorphous exchange (Tauson *et al.*, 2004, 2005). Secondary minerals with Cd as an essential component are very uncommon and result mainly from the weathering of Cd-bearing primary Zn minerals. Apart from otavite (CdCO$_3$), all known

Cd secondary minerals are restricted to one or two occurrences worldwide.

One of the few localities where an assemblage of secondary cadmium species is found is the famous Ag-Pb-Zn deposit at Broken Hill, in far western New South Wales, Australia. In 2000, specimens containing two secondary Cd minerals were collected from ore mined from the Block 14 Opencut, which had been stockpiled, for processing at the Pinnacles Mine, 15 km southwest of Broken Hill. One of the minerals proved to be goldquarryite (Roberts et al., 2003), at that time only recently approved by the International Mineralogical Association (IMA). Preliminary chemical analyses of the second mineral showed that it was an arsenate containing major Cd and Zn plus minor Cu and Mn, a composition that matched no known mineral species. Successful solution and refinement of the crystal structure showed that the mineral is a new member of the hureaulite group.

Nyholmite represents only the third known natural Cd-bearing arsenate after keyite, $Cu_3(Zn,Cu)_4Cd_2(AsO_4)_6 \cdot 2H_2O$ (Embrey et al., 1977; Cooper and Hawthorne, 1996) and andy-robertsite, $KCdCu_5(AsO_4)_4[As(OH)_2O_2]\cdot(H_2O)_2$ (Cooper et al., 1999; Cooper and Hawthorne, 2000). The mineral and the name nyholmite have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2008-047). The type specimen is deposited in the South Australian Museum, Adelaide, South Australia, (registration number G32511). The new mineral is named for Sir Ronald Sydney Nyholm (1917−1971), born at Broken Hill, New South Wales and chair and professor of Chemistry at University College, London from 1955 to 1971. The name recognizes his numerous contributions to inorganic chemistry, in particular the coordination chemistry of the transition metals, and also recognizes his Broken Hill roots.

Occurrence

The Broken Hill Ag-Pb-Zn ore body, the largest base-metal deposit in the world, is situated in the Palaeoproterozoic Willyama Supergroup of the Curnamona Craton in western New South Wales. The ore body is hosted in pelitic/psammopelitic metasediments of the Broken Hill Group that were deposited within an intracratonic rift basin between about 1680 and 1720 Ma ago (Willis et al., 1983; Stevens, 1998). The sulphide ore occurs as six stacked, stratigraphically-controlled, massive lenses of different chemistry and

mineralogy over a strike length of ~8.5 km. The oxidized zone extends to an average depth of about 75 m and is noted for its mineralogical diversity, which has resulted from the chemical complexity of the sulphide mineralization and its host rocks, and a long history of weathering and oxidation (Birch, 1990, 1999).

Particularly notable is the range of Cd-bearing secondary minerals found in the oxidized zone, which have likely formed as a result of the breakdown of Cd-bearing sphalerite (Edwards, 1955; Both, 1973). Nyholmite is the second new Cd-dominant mineral to be described from Broken Hill after birchite, $Cd_2Cu_2(PO_4)_2(SO_4)\cdot 5H_2O$ (Elliott et al., 2008). In addition, otavite, $CdCO_3$, goldquarryite, $CuCd_2Al_3(PO_4)_4F_2(H_2O)_{10}(H_2O)_2$, and niedermayrite, $Cu_4Cd(SO_4)_2(OH)_6\cdot 4H_2O$, have also been identified from Broken Hill along with a number of sulphate, phosphate and arsenate minerals, such as conichalcite-duftite, sampleite-lavendulan-zdenekite (Giester et al., 2007), christelite and serpierite, which sometimes contain significant Cd, substituting for Ca, Pb and Zn.

Although the exact area of the Block 14 Opencut that was the source of the nyholmite specimens is not known, the assemblage of arsenate minerals on the specimens indicated that they may be from a small arsenate-rich zone in the No. 2 Lens. Nyholmite occurs in cavities in a quartz-garnet-arsenopyrite matrix and is associated with spheres of pale blue goldquarryite, hemispherical aggregates of lavendulan-sampleite, druses of pale green to white scorodite-strengite and crusts of colourless gypsum.

The mineral is a late-stage supergene mineral formed under low-temperature conditions as part of a suite of secondary arsenate minerals. The following paragenesis for the suite of arsenates from the Block 14 Opencut has been proposed by Birch (1990):

carminite → corkite-hinsdalite →
     mimetite → duftite → bayldonite →
          adamite-olivenite → agardite

The overall sequence of crystallization likely represents a change from acid to more alkaline conditions (Nriagu, 1984; Williams, 1990).

Appearance, physical and optical properties

Nyholmite forms isolated white globules and tufted aggregates of fibrous crystals up to 1 mm across, and radiating hemispheres of very thin, bladed
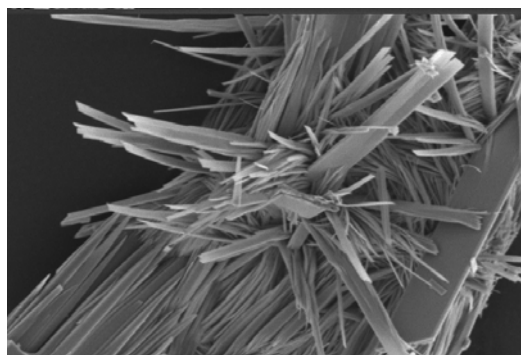
FIG. 1. SEM photomicrograph showing thin bladed colourless crystals of nyholmite with fibrous gold-quarryite crystals. The field of view is 80 μm across.

colourless crystals up to 0.5 mm across (Fig. 1). Individual crystals are up to 0.2 mm in length and 0.05 mm across. The mineral is transparent (crystals) to translucent (globules) and non-fluorescent. The streak is white, the lustre vitreous and the Mohs hardness is 3−3.5. The mineral is brittle and the fracture is uneven. No cleavage was observed. Density was not measured as the calculated densities, 4.23 g cm^{-3} for the empirical formula and 4.42 g cm^{-3} for the ideal formula, are greater than that of the heavy liquids available. One refractive index of a flat-lying crystal was obtained (β ~1.70) in white light using Cargille immersion liquids. The measurement of the

remaining refractive indices proved difficult due to the morphology of the tiny, extremely thin crystals. The Gladstone-Dale relationship (Mandarino 1981) gives a mean refractive index of 1.705 for the empirical formula. Nyholmite is slowly soluble in cold 10% hydrochloric acid.

Chemical composition

A grain of nyholmite was mounted in epoxy, polished, carbon coated and analysed with a Cameca SX51 electron microprobe operating under the following conditions in wavelength-dispersive mode: an accelerating potential of 20 kV, a probe current of 20 nA and a final beam size of 5 μm. Data were reduced using the ϕ(ρZ) method of Pouchou and Pichoir (1985). Analytical results are given in Table 1. The empirical formula, calculated on the basis of 20 oxygen atoms and water content calculated from the ideal formula from the crystal-structure solution, is $Cd_{2.80}Zn_{1.24}Mn_{0.53}Cu_{0.44}Al_{0.04}$ $Ca_{0.03}Pb_{0.02}[(AsO_4)_{3.13}(PO_4)_{0.92}]_{\Sigma4.05}$ $H_{1.91} \cdot 3.79H_2O$. The simplified formula is Cd_3Zn_2 $(AsO_3OH)_2(AsO_4)_2 \cdot 4H_2O$, which requires CdO 35.09, ZnO 14.83, As_2O_5 41.88, H_2O 8.21, total 100.00 wt.%.

X-ray powder-diffraction data

The X-ray powder-diffraction pattern for nyhol-mite (Table 2) was recorded on a 100 mm

TABLE 1. Compositional data for nyholmite.

Constituent	Wt.%	Range	Standard deviation	Probe standard
P_2O_5	6.29	5.5−6.61	0.3	hydroxylapatite
As_2O_5	34.55	33.66−35.91	0.79	gallium arsenide
Al_2O_3	0.2	0.14−0.24	0.03	almandine
MnO	3.59	3.44−3.84	0.12	rhodonite
CaO	0.16	0.13−0.19	0.02	hydroxylapatite
CuO	3.39	3.16−3.73	0.43	chalcopyrite
ZnO	9.72	9.53−10.01	0.14	sphalerite
CdO	34.58	33.81−35.26	0.15	Cd metal
PbO	0.37	0.16−0.59	0.11	crocoite
H_2O*	8.21			
Total	101.06			

Composition based on 14 analyses.
* H_2O calculated from structure determination.
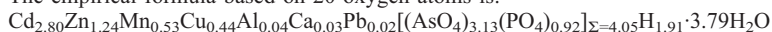The empirical formula based on 20 oxygen atoms is:
$Cd_{2.80}Zn_{1.24}Mn_{0.53}Cu_{0.44}Al_{0.04}Ca_{0.03}Pb_{0.02}[(AsO_4)_{3.13}(PO_4)_{0.92}]_{\Sigma=4.05}H_{1.91} \cdot 3.79H_2O$

TABLE 2. X-ray powder-diffraction data for nyholmite.

$I_{obs.}$	$d_{obs.}$	$I_{calc.}$	$d_{calc.}$	h	k	l
30	8.985	100	8.979	2	0	0
85	8.283	58	8.287	1	1	0
15	6.481	16	6.485	1	1	$\bar{1}$
25	6.169	7	6.175	1	1	1
		2	5.040	3	1	0
25	4.878	12	4.894	0	0	2
15	4.656	15	4.655	3	1	$\bar{1}$
10	4.491 {	5	4.505	2	0	$\bar{2}$
		26	4.489	4	0	0
10	4.296 {	8	4.324	3	1	1
		7	4.308	1	$\bar{1}$	2
10	4.207	1	4.215	0	2	1
	4.140 {	14	4.143	2	2	0
		6	4.125	1	1	2
10	3.880	6	3.885	2	2	$\bar{1}$
5	3.745	7	3.749	2	2	1
5	3.498	18	3.501	4	0	$\bar{2}$
20	3.366 {	11	3.379	0	2	2
		10	3.362	3	1	2
15	3.354	1	3.352	5	1	0
15	3.273	24	3.274	5	1	$\bar{1}$
100	3.234 {	70	3.243	2	$\bar{2}$	$\bar{2}$
		3	3.237	4	2	0
20	3.143 {	14	3.147	4	2	$\bar{1}$
		28	3.144	4	0	2
65	3.079 {	57	3.088	2	2	2
		7	3.078	5	1	1
20	2.995	26	2.993	6	0	0
45	2.976	24	2.986	1	1	3
5	2.903	5	2.905	5	$\bar{1}$	2
10	2.851	5	2.859	3	$\bar{1}$	$\bar{3}$
10	2.799	15	2.801	4	$\bar{2}$	$\bar{2}$
10	2.760	11	2.762	3	3	0
20	2.688 {	17	2.694	3	3	$\bar{1}$
		14	2.685	6	0	$\bar{2}$
15	2.667	10	2.675	0	2	3
5	2.641	9	2.645	5	1	2
5	2.635	1	2.632	3	1	3
15	2.621 {	11	2.625	3	3	1
		7	2.621	1	$\bar{3}$	2
5	2.613	6	2.608	4	2	2
5	2.574	3	2.578	1	3	2
5	2.495	4	2.496	6	2	$\bar{1}$
		3	2.460	7	1	$\bar{1}$
20	2.440 {	27	2.447	0	0	4
		1	2.439	6	0	2
10	2.419	12	2.428	2	0	$\bar{4}$
5	2.389	3	2.389	6	2	1
5	2.350	10	2.353	5	3	0
5	2.342	11	2.341	7	$\bar{1}$	1
5	2.335	5	2.335	0	4	0
		2	2.328	6	2	$\bar{2}$

$I_{obs.}$	$d_{obs.}$	$I_{calc.}$	$d_{calc.}$	h	k	l
5	2.306	9	2.306	7	1	$\bar{2}$
		5	2.284	3	1	$\bar{4}$
5	2.271	0	2.272	0	4	1
		5	2.256	1	3	$\bar{3}$
10	2.249 {	7	2.253	4	0	$\bar{4}$
		1	2.252	5	3	1
10	2.246	23	2.245	8	0	0
10	2.209 {	5	2.215	1	3	3
		0	2.214	4	2	3
5	2.186 {	5	2.189	2	4	1
		2	2.181	5	$\bar{3}$	2
5	2.155	3	2.154	2	$\bar{2}$	4
		6	2.127	3	1	4
5	2.120	1	2.121	7	1	2
		4	2.078	7	1	$\bar{3}$
5	2.070	5	2.072	4	4	0
5	2.066	0	2.064	5	3	2
		4	2.058	3	3	3
		9	2.057	4	0	4
5	2.048	0	2.048	4	4	$\bar{1}$
5	2.023 {	4	2.029	4	$\bar{2}$	$\bar{4}$
		2	2.023	8	2	0
		3	2.003	6	0	$\bar{4}$
		4	1.980	7	3	0
		3	1.975	5	3	$\bar{3}$
5	1.973	1	1.973	7	3	$\bar{1}$
		3	1.962	8	0	2
		2	1.944	8	2	1
		1	1.883	4	2	4
		2	1.882	2	$\bar{4}$	3
5	1.875	0	1.875	4	4	2
		3	1.841	6	4	0
5	1.828	4	1.829	1	$\bar{5}$	$\bar{1}$
5	1.824 {	2	1.822	1	$\bar{5}$	1
		5	1.809	8	2	2
		4	1.802	6	0	4
		7	1.788	3	3	4
		2	1.785	7	3	2
5	1.782	3	1.783	3	5	0
		7	1.759	5	$\bar{3}$	$\bar{4}$
		2	1.758	9	$\bar{1}$	$\bar{3}$
5	1.754	7	1.751	8	0	$\bar{4}$
5	1.728	3	1.731	1	5	2
		4	1.693	3	$\bar{5}$	2
		7	1.689	0	4	4
		2	1.687	6	4	2
10	1.681	9	1.681	9	3	$\bar{1}$
		3	1.680	9	3	0
5	1.650	5	1.651	6	4	$\bar{3}$
		2	1.639	8	$\bar{2}$	$\bar{4}$
		5	1.637	0	2	$\bar{2}$
		5	1.637	1	$\bar{3}$	5
		5	1.636	2	0	$\bar{6}$

Intensities estimated visually. $I_{calc.}$ computed from the crystal structure model.

Guinier-Hägg camera using monochromatic Cr-$K\alpha$ radiation (λ 2.28970 Å). The film was scanned using a film scanner, the powder-diffraction profile was extracted and peak positions were calibrated using an internal silicon standard (NBS SRM 640a). The intensities were visually estimated and the calculated intensities were obtained from the structural model (Yvon *et al.*, 1977). Unit-cell refinement using the Le Bail profile-fitting method (Le Bail *et al.*, 1988), starting from the unit-cell parameters determined using single-crystal methods, gave the following parameters: a = 18.042(2) Å, b = 9.315(1) Å, c = 9.797(1) Å, β = 96.14(1)°, V = 1637.2(2) Å^3, which agree with those refined using single-crystal methods.

Crystal structure determination and refinement

The tiny, extremely thin crystals of nyholmite proved too small to provide more than several weak reflections per frame using a CCD-based diffractometer. Hence X-ray intensity data were obtained at the ChemMatCARS (CARS = Consortium for Advanced Radiation Sources) facility of the Advanced Photon Source of the Argonne National Laboratory, Argonne, USA. Data were collected from a crystal measuring 0.050 mm × 0.010 mm × 0.003 mm on a modified 3-circle diffractometer using a Bruker SMART-6000 CCD detector and a wavelength of 0.49594 Å. Data were integrated and corrected for Lorentz, polarization, and background effects. No absorption correction was applied. Experimental details are listed in Table 3.

The systematic absences were consistent with space groups Cc (non centrosymmetric) and $C2/c$ (centrosymmetric); however, the mean value of $|E^2-1|$ of 0.816 did not give a conclusive indication of the presence of a centre of symmetry. Starting with the atomic coordinates of hureaulite (Moore and Araki, 1973), the structure was refined in $C2/c$ (*SHELXL-97*, Sheldrick, 1997; *WinGX*, Farrugia 1999). Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson 1992). The structure model including anisotropic-displacement parameters for all atoms converged to an agreement index ($R1$) of 3.73%, calculated for the 2045 observed unique reflections ($F_0 > 4\sigma F$). The locations of the H atoms in the unit cell could not be determined. Positional and anisotropic-displacement parameters are

given in Table 4, selected interatomic distances in Table 5, and a bond-valence analysis in Table 6.

Structure description

Cation coordination

The asymmetric unit contains three octahedrally coordinated sites (M), two tetrahedrally coordinated sites (T), ten O atoms and five H atoms. All are on general positions with the exception of $M(1)$, which is on a twofold rotation axis at $(0, y, ¼)$.

Each of the three M positions is coordinated by six anions in a distorted-octahedral arrangement. A refinement of the Cd:Zn ratio of the $M(1)$ site implies an occupancy of $Cd_{0.73}Zn_{0.27}$. The calculated $<M-O>$ distance using this occupancy of 2.250 Å (ionic radii from Shannon 1976) agrees with the observed value of 2.251 Å. Occupancy refinement of the $M(2)$ site, using the Zn scattering factor, gave a value of 1.207(5), which implies partial occupancy by a heavier atom. The $M(2)$ site exhibits a greater bond-length distortion than that of the $M(1)$ and $M(3)$ sites, so it would be expected that the presence in the formula of 0.44 a.p.f.u. (atoms per formula unit) Cu^{2+}, a Jahn-Teller distorting cation, would have a preference for this site. The average $M(2)-O$ bond length, of 2.155 Å, is compatible with the occupancy of the site by $Zn_{0.31}Cu_{0.22}Cd_{0.19}Mn_{0.26}Al_{0.02}$. Refinement of the occupancy of the $M(3)$ site, using the Cd scattering factor, gave a value of 0.979(5), showing that it must be almost completely occupied by Cd, plus minor Zn, Pb and Ca. The observed $<M-O>$ length of 2.292 Å is in accord with an occupancy of $Cd_{0.89}Zn_{0.08}Ca_{0.01}Pb_{0.02}$.

These assignments give a total octahedral-site population of $Cd_{2.90}Zn_{1.06}Mn_{0.52}Cu_{0.43}Al_{0.04}Ca_{0.03}Pb_{0.02}$, which has a greater Cd:(Zn+Mn+Cu) ratio than that of the empirical formula derived from the chemical analysis. This suggested a chemical variability between nyholmite crystals and globules, which was in fact confirmed by SEM-EDS analyses of several minute crystals showing that they have variable and often higher Cd content than the globules.

The two T sites are both occupied by As and P, and coordinated by four anions in a distorted-tetrahedral arrangement. Average $T-O$ bond lengths for the $T(1)$- and $T(2)$-centred tetrahedra of 1.640 and 1.671 Å, respectively, are consistent with the majority of the P being located at the $T(1)$ site. A refinement of the occupancies of the $T(1)$

and $T(2)$ sites gave As:P ratios of 0.66(9):0.34(9) and 0.83(9):0.17(9) respectively. The $T(2)O_4$ group is an acid $(As,P)(O,OH)_4$ group with the $(As,P)-OH$ bond (1.689 Å) being considerably longer than the three $(As,P)-O$ bonds (average 1.665 Å) which is typical for protonated AsO_4 tetrahedra (Ferraris and Ivaldi 1984).

Stucture topology

The structure of nyholmite is characterized by a kinked, short, five-membered chain or pentamer, of composition $M_5\phi_{22}$ [ϕ: O^{2-}, H_2O] that extends

in the a direction. An $M(1)O_6$ octahedron links by edge-sharing to two $M(3)O_6$ octahedra, which in turn each shares edges with an $M(2)O_6$ octahedron. The pentamers link by sharing corners, *via* the O(1) and O(5) atoms, to form a sheet in the (001) plane. Further linkage between pentamers is provided by corner-sharing AsO_4 groups, to form thick slabs in the (001) plane (Fig. 2). The slabs link in the c direction by corner-sharing between octahedra and tetrahedra to form a densely packed heteropolyhedral framework (Fig. 3). Interstitial channels within the framework extend along the c direction and are occupied by the hydrogen atoms

TABLE 3. Crystal data, data collection and refinement details for nyholmite.

Crystal data
Formula	$Cd_{2.90}Zn_{1.06}Mn_{0.52}Cu_{0.43}Al_{0.04}Ca_{0.02}Pb_{0.03}$ $[(AsO_4)_{3.57}(PO_4)_{0.43}]_{\Sigma4.00}H_2 \cdot 4H_2O$
Space group	$C2/c$
a,b,c (Å)	18.062(4), 9.341(2), 9.844(2)
β (º)	96.17(3)
V (Å³); Z	1651.2(6); 4
$F(000)$	2034
μ (mm^{-1})	14.671
Crystal dimensions (mm)	$0.050 \times 0.010 \times 0.003$

Data collection
Diffractometer	SMART 6000 detector mounted on a Bruker Kappa Platform
Temperature (K)	123
Wavelength	$\lambda = 0.49594$ Å
θ range (º)	2.46 to 30.35
Detector distance (mm)	50
Rotation axes, width (º)	ϕ, ω
Total no. of frames	690
Collection time per frame (s)	1
Index ranges	$-25 \leqslant h \leqslant 25, -13 \leqslant k \leqslant 13, -12 \leqslant l \leqslant 13$
Total reflections measured	8668
Data completeness (%)	85.8
Unique reflections	2127 ($R_{\text{int}} = 4.84\%$)

Refinement
Refinement on	F^2
$R1^*$ for $F_o > 4\sigma(F)$	3.73%
$wR2^{**}$ for all F_o^2	8.61%
Reflections used [$F_o^2 > 4\sigma(F_o^2)$]	2045
Number of parameters refined	138
Extinction factor	0.00000(10)
$(\Delta/\sigma)_{\text{max}}$	0.0001
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ (e/Å³)	1.49, -0.88
Goodness of Fit	1.081

* $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$
** $wR2 = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2)^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.042 \text{ P})^2 + 12.60 \text{ P}]$;
P = ([max of (0 or F_0^2)] + $2F_c^2$)/3

TABLE 4. Fractional coordinates and displacement parameters (Å^2) for atoms for nyholmite.

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$M(1)$	0	−0.10841(7)	0.25	0.0156(3)	0.0164(4)	0.0107(4)	0.0194(4)	0	0.0006(3)	0
$M(2)$	0.31675(3)	0.08527(6)	0.68608(7)	0.0182(2)	0.0215(3)	0.0109(3)	0.0219(4)	0.0034(2)	0.0008(2)	−0.0004(2)
$M(3)$	0.17497(2)	0.02916(4)	0.36559(5)	0.01732(16)	0.0180(2)	0.0125(2)	0.0215(3)	−0.00237(15)	0.00223(16)	−0.00115(14)
$T(1)$	0.08304(3)	0.18435(6)	0.08981(7)	0.0130(2)	0.0146(3)	0.0094(3)	0.0148(4)	−0.0009(2)	0.0006(2)	0.0015(2)
$T(2)$	0.16130(3)	0.26692(6)	0.62387(6)	0.0133(2)	0.0149(3)	0.0070(3)	0.0172(3)	−0.00037(19)	−0.0012(2)	0.00044(18)
$O(1)$	0.1589(2)	0.2739(5)	0.1356(5)	0.0257(9)	0.024(2)	0.026(2)	0.027(2)	−0.0025(17)	0.0006(17)	−0.0044(16)
$OH(2)$	0.0109(3)	0.2964(5)	0.0791(5)	0.0310(11)	0.035(3)	0.029(2)	0.028(2)	−0.0086(18)	−0.0015(19)	0.0080(19)
$O(3)$	0.0755(2)	0.0663(5)	0.2090(5)	0.0270(10)	0.025(2)	0.022(2)	0.034(3)	0.0081(18)	0.0009(18)	−0.0036(16)
$O(4)$	0.0840(2)	0.1111(5)	−0.0615(4)	0.0260(9)	0.024(2)	0.029(2)	0.024(2)	−0.0045(17)	0.0019(17)	0.0102(17)
$O(5)$	0.1656(2)	0.2490(4)	0.4541(4)	0.0232(9)	0.029(2)	0.0184(18)	0.021(2)	−0.0039(15)	−0.0023(16)	0.0014(16)
$O(6)$	0.0725(2)	0.2749(4)	0.6557(5)	0.0241(9)	0.0205(19)	0.0174(18)	0.033(2)	−0.0020(17)	−0.0007(17)	0.0000(15)
$O(7)$	0.2054(2)	0.4160(4)	0.6779(5)	0.0216(9)	0.0193(19)	0.0159(17)	0.031(2)	−0.0025(15)	0.0084(16)	−0.0019(14)
$O(8)$	0.2048(2)	0.1281(4)	0.7023(5)	0.0247(9)	0.024(2)	0.0143(17)	0.036(2)	0.0076(16)	0.0051(17)	0.0017(15)
$H_2O(9)$	0.4176(3)	−0.0033(5)	0.6613(6)	0.0364(12)	0.033(3)	0.031(2)	0.045(3)	0.015(2)	0.003(2)	−0.008(2)
$H_2O(10)$	0.2604(2)	−0.0841(4)	0.5323(4)	0.0240(9)	0.026(2)	0.0220(19)	0.025(2)	0.0046(16)	0.0077(17)	0.0021(16)

The anisotropic-displacement parameters (U_{ij}) are defined as exp$[-2\pi^2\Sigma_{i=1}^{3}\Sigma_{\phi=1}^{3}jU_{ij}a_i^*\,a_j^*\,h_ih_j]$

TABLE 5. Selected interatomic distances (Å), angles (º) and suggested hydrogen bonds for nyholmite.

$M(1)-O(3)$ ×2	2.192(4)	$M(2)-H_2O(9)$	2.039(5)
$M(1)-O(4)$ ×2	2.267(4)	$M(2)-O(8)$	2.084(4)
$M(1)-O(6)$ ×2	2.293(4)	$M(2)-O(5)$	2.121(4)
$<M-O>$	2.251	$M(2)-O(7)$	2.138(4)
		$M(2)-O(1)$	2.200(4)
$M(3)-O(5)$	2.244(4)	$M(2)-H_2O(10)$	2.345(5)
$M(3)-O(3)$	2.265(5)	$<M-O>$	2.155
$M(3)-O(4)$	2.277(4)		
$M(3)-O(8)$	2.285(4)		
$M(3)-O(7)$	2.305(4)		
$M(3)-H_2O(10)$	2.377(4)		
$<M-O>$	2.292		
$T(1)-O(1)$	1.626(4)	$T(2)-O(8)$	1.663(4)
$T(1)-O(3)$	1.627(4)	$T(2)-O(7)$	1.663(4)
$T(1)-O(4)$	1.641(4)	$T(2)-O(6)$	1.669(4)
$T(1)-OH(2)$	1.666(5)	$T(2)-O(5)$	1.689(4)
$<T-O>$	1.64	$<T-O>$	1.671
$O(3)-M(1)-O(3)$	83.7(2)	$H_2O(9)-M(2)-O(8)$	166.80(18)
$O(3)-M(1)-O(4)$	77.54(16)	$H_2O(9)-M(2)-O(5)$	91.14(18)
$O(3)-M(1)-O(4)$	103.44(17)	$O(8)-M(2)-O(5)$	97.15(16)
$O(3)-M(1)-O(4)$	103.44(17)	$H_2O(9)-M(2)-O(7)$	90.26(17)
$O(3)-M(1)-O(4)$	77.54(16)	$O(8)-M(2)-O(7)$	81.10(16)
$O(4)-M(1)-O(4)$	178.7(2)	$O(5)-M(2)-O(7)$	177.51(17)
$O(3)-M(1)-O(6)$	92.11(16)	$H_2O(9)-M(2)-O(1)$	103.49(19)
$O(3)-M(1)-O(6)$	166.72(17)	$O(8)-M(2)-O(1)$	86.38(17)
$O(4)-M(1)-O(6)$	87.88(16)	$O(5)-M(2)-O(1)$	92.96(16)
$O(4)-M(1)-O(6)$	91.25(15)	$O(7)-M(2)-O(1)$	88.71(17)
$O(3)-M(1)-O(6)$	166.72(17)	$O(9)-M(2)-H_2O(10)$	88.86(18)
$O(3)-M(1)-O(6)$	92.11(16)	$O(8)-M(2)-H_2O(10)$	79.73(16)
$O(4)-M(1)-O(6)$	91.25(15)	$O(5)-M(2)-H_2O(10)$	99.06(15)
$O(4)-M(1)-O(6)$	87.88(16)	$O(7)-M(2)-H_2O(10)$	78.92(16)
$O(6)-M(1)-O(6)$	94.6(2)	$O(1)-M(2)-H_2O(10)$	162.62(15)
$O(5)-M(3)-O(3)$	92.11(16)	$O(1)-T(1)-O(3)$	106.4(2)
$O(5)-M(3)-O(4)$	108.48(16)	$O(1)-T(1)-O(4)$	112.0(2)
$O(3)-M(3)-O(4)$	75.88(15)	$O(3)-T(1)-O(4)$	112.5(2)
$O(5)-M(3)-O(8)$	153.50(15)	$O(1)-T(1)-OH(2)$	108.9(2)
$O(3)-M(3)-O(8)$	81.35(17)	$O(3)-T(1)-OH(2)$	110.3(2)
$O(4)-M(3)-O(8)$	94.87(16)	$O(4)-T(1)-OH(2)$	106.8(2)
$O(5)-M(3)-O(7)$	88.85(15)	$<O-T(1)-O>$	109.48
$O(3)-M(3)-O(7)$	122.03(16)		
$O(4)-M(3)-O(7)$	155.38(15)	$O(8)-T(2)-O(7)$	108.5(2)
$O(8)-M(3)-O(7)$	73.46(14)	$O(8)-T(2)-O(6)$	111.3(2)
$O(5)-M(3)-H_2O(10)$	102.09(15)	$O(7)-T(2)-O(6)$	109.9(2)
$O(3)-M(3)-H_2O(10)$	161.24(15)	$O(8)-T(2)-O(5)$	108.2(2)
$O(4)-M(3)-H_2O(10)$	87.91(15)	$O(7)-T(2)-O(5)$	109.2(2)
$O(8)-M(3)-H_2O(10)$	90.85(15)	$O(6)-T(2)-O(5)$	109.7(2)
$O(7)-M(3)-H_2O(10)$	71.04(15)	$<O-T(2)-O>$	109.47

Atomic separations corresponding to possible hydrogen−bonds

$H_2O(10)\cdots O(1)$	2.671	$H_2O(9)\cdots O(6)$	2.739
$H_2O(10)\cdots O(1)$	2.818	$OH(2)\cdots H_2O(9)$	2.747
$H_2O(9)\cdots OH(2)$	2.743		

TABLE 6. Bond-valence analysis for nyholmite.

	$M(1)$	$M(2)$	$M(3)$	$T(1)$	$T(2)$	H(1)	H(2)	H(3)	H(4)	H(5)	Sum (excl. H)	Sum (incl. H)
O(1)		0.31		1.30					0.21	0.17	1.63	2.01
OH(2)				1.16		0.81	0.19				1.19	2.19
O(3)	0.41↓→ 0.41→		0.37	1.29							2.10	2.10
O(4)	0.33↓→ 0.33↓		0.36	1.25							1.96	1.96
O(5)		0.38	0.39		1.16						1.96	1.96
O(6)	0.31↓→ 0.31→				1.23			0.19			1.57	1.76
O(7)		0.36	0.33		1.25						1.97	1.97
O(8)		0.42	0.35		1.25						2.05	2.05
$H_2O(9)$		0.47				0.19	0.81	0.81			0.47	2.28
$H_2O(10)$		0.21	0.27						0.79	0.83	0.48	2.10
Sum	2.10	2.15	2.07	5.00	4.89	1.00	1.00	1.00	1.00	1.00		

Sums for the M and T sites calculated using occupancies of:
$M(1) = Cd_{0.73}Zn_{0.27}$;
$M(2) = Zn_{0.31}Cu_{0.22}Cd_{0.19}Mn_{0.26}Al_{0.02}$;
$M(3) = Cd_{0.89}Zn_{0.08}Ca_{0.01}Pb_{0.02}$;
$T(1) = As_{0.66}P_{0.34}$;
$T(2) = As_{0.83}P_{0.17}$.
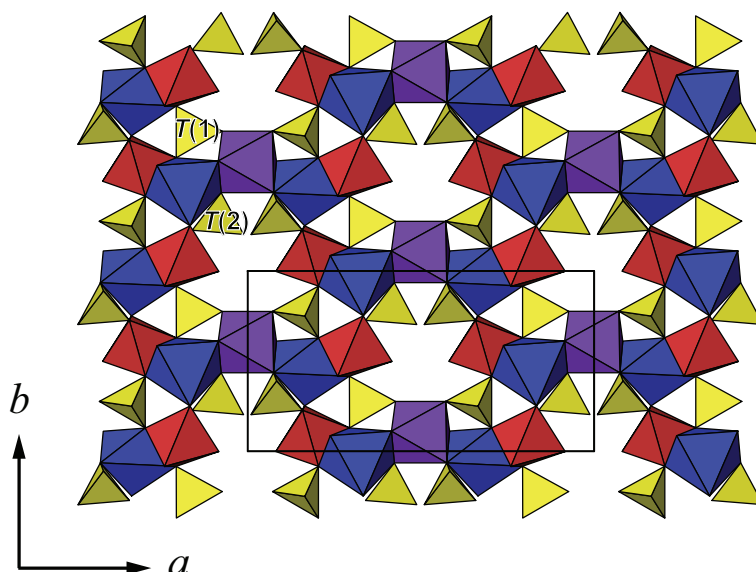
FIG. 2. The crystal structure of nyholmite viewed along [001] (the unit cell is outlined). $M(1)\phi_6$ octahedra are shaded purple, $M(2)\phi_6$ octahedra are shaded red and $M(3)\phi_6$ octahedra are shaded blue. All structure drawings were completed using *ATOMS* (Shape Software 1997).
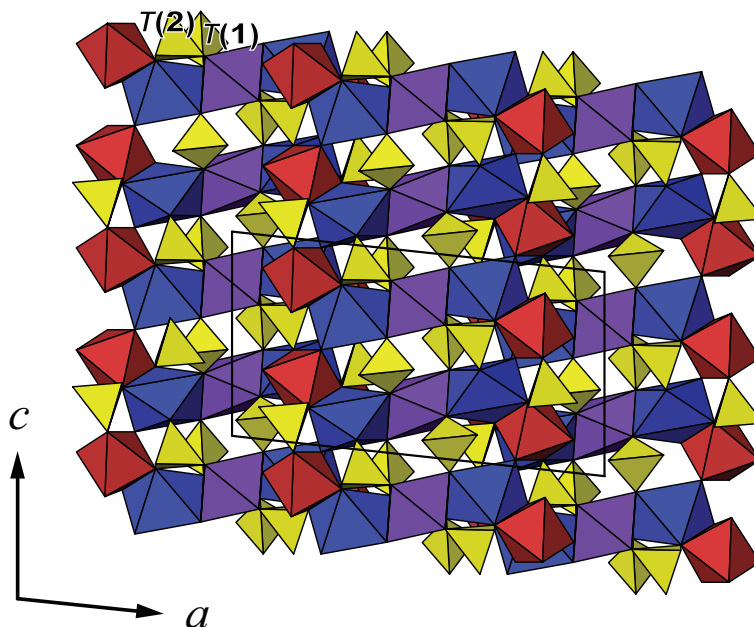
FIG. 3. The crystal structure of nyholmite viewed along [010] (the unit cell is outlined).

of the OH(2) and $H_2O(9)$ groups which coordinate to the *M* and *T* cations.

Hydrogen bonding

The bond-valence analysis (Table 6) indicates that there is one OH group and two H_2O groups in the nyholmite structure. There are seven sites occupied by O^{2-} anions, with incident bond-valences from 1.57 to 2.10 v.u. The O(1) (v.u. = 1.63) and O(6) (v.u. = 1.57) anions are fairly undersaturated so are likely hydrogen-bond acceptors.

Based on stereochemical considerations the $H_2O(9)$ group likely donates hydrogen bonds that are accepted by OH(2) and O(6) with O···O distances of 2.742 and 2.739 Å respectively. A hydrogen bond donated by the OH(2) group is likely accepted by $H_2O(9)$ and hydrogen bonds donated by the $H_2O(10)$ group are likely accepted by two O(1) anions. These implied hydrogen bonds are of moderate to weak strength.

Related structures

Nyholmite is isostructural with the minerals of the hureaulite group: hureaulite, $Mn_5^{2+}(PO_3OH)_2(PO_4)_2 \cdot 4H_2O$; sainfieldite,

$Ca_5(AsO_3OH)_2(AsO_4)_2 \cdot 4H_2O$; villyaellenite, $(Mn^{2+},Ca,Zn)_5(AsO_3OH)_2(AsO_4)_2 \cdot 4H_2O$. Crystal-structure descriptions of hureaulite have been published for both natural and synthetic crystals (Moore and Araki, 1973; Menchetti and Sabelli, 1973; de Amorim *et al.*, 1996). The structure of villyaellenite has been determined from both natural and synthetic material by Kampf and Ross (1988) and Stock *et al.* (2002) respectively, and the structure of sainfeldite was solved by Ferraris and Abbona (1972). Three isostructural synthetic compounds are also known: $Cd_5(PO_3OH)_2(PO_4)_2 \cdot 4H_2O$ (Ropp and Mooney, 1960; Averbuch-Pouchot and Durif, 1970; Hideki *et al.*, 1976), $Cd_5(AsO_3OH)_2(AsO_4)_2 \cdot 4H_2O$ (Averbuch-Pouchot and Durif, 1970; Johnson *et al.*, 2003) and $Fe_5^{2+}(PO_3OH)_2(PO_4)_2 \cdot 4H_2O$ (Bustamante *et al.*, 2005). Table 7 gives a comparison of relevant data.

Only limited composition ranges have been reported for the minerals of the hureaulite group. Villyaellenite from the type locality, the Sainte-Marie aux Mines, Haut-Rhin, France, has a composition near the midpoint of the villyaellenite-sainfeldite series (Sarp, 1984). However, no structural information is available so the extent of ordering of Ca and Mn in the structure is not known. The structure of villyaellenite was solved

TABLE 7. Comparison of related minerals and compounds.

Mineral/Compound	Nyholmite	Hureaulite	Sainfeldite	Villyaellenite	Synthetic	Synthetic	Synthetic
Formula	$Cd_2Zn_2(AsO_3OH)_2(AsO_4)_2 \cdot 4H_2O$	$Mn_5^{2+}(PO_3OH)_2(PO_4)_2 \cdot 4H_2O$	$Ca_5(AsO_3OH)_2(AsO_4)_2 \cdot 4H_2O$	$Mn_5(AsO_3OH)_2(AsO_4)_2 \cdot 4H_2O$	$Cd_5(AsO_3OH)_2(AsO_4)_2 \cdot 4H_2O$	$Cd_5(PO_3OH)_2(PO_4)_2 \cdot 4H_2O$	$Fe_5^{2+}(PO_3OH)_2(PO_4)_2 \cdot 4H_2O$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$
a (Å)	18.062(4)	17.594(10)	18.781(7)	18.015(5)	18.382(2)	17.887(6)	17.487(4)
b (Å)	9.341(19)	9.086(5)	9.820(4)	9.261(2)	9.7192(13)	9.394(3)	9.017(2)
c (Å)	9.844(2)	9.404(5)	10.191(4)	9.770(3)	9.9791(13)	9.675(3)	9.338(2)
β (°)	96.17(3)	96.67(8)	97.02	96.238(7)	96.369(3)	96.59(2)	96.27(3)
V (Å³)	1651.2(6)	1493.14	1865.43	1620.3	1771.9(4)	1614.95	1463.6(6)
Z	4	4	4	4	4	4	4
Reference	this work	Moore and Araki (1973)	Ferraris and Abbona (1972)	Kampf and Ross (1988)	Johnson et al. 2003	Hideki et al. (1976)	Bustamente et al. (2005)

using a crystal from Mapimi, Mexico, of near end-member composition, but containing minor amounts of Zn and Ca (Kampf and Ross, 1988). Based on bond distances and refined site occupancies, these authors suggest that Zn is preferentially contained in the Mn(2) site and Ca in the Mn(3) site in the structure. Paragenetic evidence also supports some degree of ordering of Mn and Ca in type villyaellenite, but suggests that a complete solid solution may not exist. In the nyholmite structure, Ca is also partitioned into the $M(3)$ site, as is Pb, and structural evidence also suggests at least a partial ordering of Cd and Zn, plus Cu, in the $M(1)$ and $M(2)$ sites.

Acknowledgements

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