

HYDROGEN BONDING IN THE CRYSTAL STRUCTURE OF LEGRANDITE: $\text{Zn}_2(\text{AsO}_4)(\text{OH})(\text{H}_2\text{O})$

FRANK C. HAWTHORNE[§] & YASSIR A. ABDU

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

KIMBERLY T. TAIT

Department of Natural History, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6, Canada

ABSTRACT

The crystal structure of legrandite -- $\text{Zn}_2(\text{AsO}_4)(\text{OH})(\text{H}_2\text{O})$, monoclinic, a 12.8052(3), b 7.9249(2), c 10.2173(2) Å, β 104.4329(3)°, V 1004.13(6) Å³, space group $P2_1/c$, $Z = 2$ -- has been refined to an R_1 value of 1.2% based on 2844 unique [$|F_o| > 4\sigma(F)$] reflections measured with a Bruker D8 three-circle diffractometer equipped with a rotating-anode generator (MoK α X-radiation), multilayer optics, and an APEX-II detector. The legrandite structure is a heteropolyhedral framework of (AsO₄) tetrahedra, (Zn ϕ_5) square pyramids, and (Zn ϕ_6) octahedra [$\phi = \text{O}, (\text{OH}), (\text{H}_2\text{O})$] with extensive hydrogen bonding across its interstices. All hydrogen positions were located, all hydrogen bonds were assigned, and the H...O distances are in reasonable accord with the published relation between O–H stretching frequency and H...O bond-length.

Keywords: legrandite, crystal-structure, electron-microprobe analysis, hydrogen bonding.

INTRODUCTION

There has been much work in the last twenty years on developing hierarchical classifications of oxysalt minerals (Hawthorne 1984, 1985, 1986, 1990, 1997, Sabelli & Trosti-Ferroni 1985, Hawthorne *et al.* 1996, 2000, Hawthorne & Huminicki 2002, Huminicki & Hawthorne 2002, Burns 1999, Burns *et al.* 1996, Krivovichev 2005, 2008, Krivovichev & Filatov 1999), focusing on the bond topology of the more strongly bonded cations. With much of this work now in place for minerals, it is important to focus on the bond topology of the interstitial species (*e.g.*, Schindler & Hawthorne 2001a,b,c, 2004, 2008, Schindler *et al.* 2006). It is the interstitial bonds that control the stability of minerals, as these weak bonds are more easily broken with changing conditions than the stronger bonds of the structural unit. Hydrogen bonds are of particular importance in this regard, and the stabilities of a large number of oxysalt minerals are controlled by the weak hydrogen bonds that bind their structural units together. Consequently, it is important to determine the details of hydrogen bonding in oxysalt minerals if we are to understand the details of their stability and the mechanisms by which they break down. With this as

background, here we describe the pattern of hydrogen bonding in legrandite.

EXPERIMENTAL

The crystal used in this work comes from the Tsumeb mine, Otjikoto (Oshikoto) region, Namibia, and was taken from the holotype sample for ianbruceite (Cooper *et al.* 2012), which has been deposited in the mineral collection of the Department of Natural History, Royal Ontario Museum, catalogue number M53150.

Collection of X-ray intensity data

A single crystal (15 × 20 × 30 µm) on a tapered glass fiber was mounted on a Bruker D8 three-circle diffractometer equipped with a rotating-anode generator (MoK α), multilayer optics, and an APEX-II detector. A total of 35,978 intensities (11,330 within the Ewald sphere) was collected to 60° 2 θ using 10 s per 0.2° frames with a crystal-to-detector distance of 5 cm. Empirical absorption corrections (SADABS; Sheldrick 2008) were applied and equivalent reflections were then corrected for Lorentz, polarization, and background effects, averaged and reduced to structure factors. The

[§] E-mail address: Frank.Hawthorne@ad.umanitoba.ca

unit cell dimensions were obtained by least-squares refinement of the positions of 9847 reflections with $I > 10\sigma(I)$ and are given in Table 1, together with other information pertaining to data collection and structure refinement.

Crystal-structure refinement

All calculations were done with the SHELXTL PC (Plus) suite of programs. Systematic absences in the single-crystal X-ray diffraction data are consistent with space group $P2_1/c$, and the structure was solved with this symmetry. Crystal-structure refinement was initiated with the atom coordinates of McLean *et al.* (1971), and the structure was refined by full-matrix least-squares to an R_1 index of 1.2%. At the final stages of refinement, six H (hydrogen) sites were identified in difference-Fourier maps and were inserted into the refinement. The O(donor)–H distances were softly constrained to be close to 0.98 Å and the H–H distances were softly constrained to be close to 1.59 Å during refinement. Refined atom coordinates and anisotropic-displacement parameters are listed in Table 2, selected interatomic distances are given in Table 3, and bond valences, calculated with the parameters of Brown and Altermatt (1985), are given in Table 4. Bond-valences for hydrogen bonds were calculated from the curve of Brown (1976). A table of structure-factors and a cif file may be obtained from The Depository of Unpublished

Data, on the MAC website [document Legrandite CM_233].

Electron-microprobe analysis

Several crystals of legrandite of differing shades of blue were mounted in epoxy on 2.5 cm diameter

TABLE 1. MISCELLANEOUS REFINEMENT DATA FOR LEGRANDITE

<i>a</i> (Å)	12.8052(3)
<i>b</i>	7.9249(2)
<i>c</i>	10.2173(2)
β (°)	104.4329(3)
<i>V</i> (Å ³)	1004.13(6)
Space group	$P2_1/c$
<i>Z</i>	2
<i>D</i> _{calc.} (g/cm ³)	4.030
Radiation/filter	MoK α /graphite
2 θ -range for data collection (°)	60.00
<i>R</i> (int) (%)	1.23
Reflections collected	35978
Independent reflections	2943
<i>F</i> _o > 4 σ <i>F</i>	2844
Final <i>R</i> (obs) (%)	<i>R</i> ₁ = 1.23
[<i>F</i> _o > 4 σ <i>F</i>]	
<i>R</i> indices (all data) (%)	<i>R</i> ₁ = 1.34 <i>wR</i> ₂ = 5.01 <i>Goof</i> = 1.334

TABLE 2. ATOM POSITIONS AND DISPLACEMENT PARAMETERS (Å²) FOR LEGRANDITE

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	<i>U</i> _{eq}
As(1)	0.14963(2)	0.05491(3)	0.21980(2)	0.00802(10)	0.00822(10)	0.00689(10)	−0.00034(7)	0.00203(7)	−0.00007(7)	0.00768(6)
As(2)	0.38529(2)	0.42165(3)	0.21410(2)	0.00833(10)	0.00779(10)	0.00740(10)	0.00019(7)	0.00278(7)	0.00002(7)	0.00770(6)
Zn(1)	0.40327(2)	0.04976(3)	0.38962(3)	0.01089(12)	0.01209(13)	0.01040(12)	0.00014(9)	0.00185(9)	0.00177(9)	0.01127(6)
Zn(2)	0.25255(2)	0.33083(3)	0.46242(3)	0.01025(12)	0.00927(12)	0.01152(12)	−0.00071(9)	0.00282(9)	0.00041(9)	0.01033(6)
Zn(3)	0.36202(2)	0.80578(3)	0.12765(3)	0.01449(13)	0.01042(12)	0.01209(12)	0.00182(9)	0.00046(10)	−0.00093(9)	0.01284(6)
Zn(4)	0.01007(2)	0.24192(4)	0.44038(3)	0.01113(12)	0.01557(13)	0.01250(13)	−0.00073(10)	0.00259(10)	−0.00091(9)	0.01313(7)
O(1)	0.26801(14)	0.9532(2)	0.26147(18)	0.0100(7)	0.0124(8)	0.0145(8)	−0.0022(6)	0.0005(6)	0.0030(6)	0.0127(3)
O(2)	0.13880(13)	0.1602(2)	0.07322(16)	0.0108(7)	0.0165(8)	0.0094(7)	0.0049(6)	0.0035(6)	0.0021(6)	0.0121(3)
O(3)	0.13303(13)	0.1895(2)	0.34154(17)	0.0114(7)	0.0152(8)	0.0127(7)	−0.0065(6)	0.0047(6)	−0.0019(6)	0.0128(3)
O(4)	0.04897(14)	0.9126(2)	0.20262(17)	0.0133(8)	0.0137(8)	0.0127(8)	−0.0023(6)	0.0036(6)	−0.0049(6)	0.0132(3)
O(5)	0.47910(13)	0.9513(2)	0.24071(17)	0.0090(7)	0.0164(8)	0.0129(7)	−0.0043(6)	0.0012(6)	0.0020(6)	0.0131(3)
O(6)	0.35330(14)	0.3422(2)	0.05675(16)	0.0178(8)	0.0168(8)	0.0085(7)	−0.0037(6)	0.0047(6)	−0.0080(7)	0.0141(3)
O(7)	0.34595(14)	0.2901(2)	0.31982(17)	0.0151(8)	0.0102(7)	0.0131(7)	0.0034(6)	0.0078(6)	0.0009(6)	0.0120(3)
O(8)	0.32021(15)	0.6062(2)	0.21800(18)	0.0220(9)	0.0096(7)	0.0193(8)	0.0037(6)	0.0124(7)	0.0051(7)	0.0157(3)
O(9)	0.07895(17)	0.5313(3)	0.1396(2)	0.0233(10)	0.0217(10)	0.0290(10)	0.0092(8)	0.0117(8)	0.0059(8)	0.0238(4)
O(10)	0.44584(14)	0.6626(2)	0.01455(17)	0.0128(7)	0.0112(7)	0.0116(7)	0.0002(6)	0.0037(6)	0.0003(6)	0.0118(3)
O(11)	0.27353(14)	0.5767(2)	0.46950(17)	0.0141(8)	0.0111(7)	0.0108(7)	−0.0009(6)	0.0040(6)	−0.0024(6)	0.0119(3)
O(12)	0.08807(16)	0.7338(3)	0.4346(2)	0.0199(9)	0.0294(10)	0.0193(9)	0.0088(8)	0.0101(7)	0.0090(8)	0.0219(4)
H(1)	0.461(4)	0.748(4)	−0.047(4)	0.05						
H(2)	0.267(4)	0.622(6)	0.379(2)	0.05						
H(3)	0.1576(4)	0.543(6)	0.163(5)	0.05						
H(4)	0.054(4)	0.468(5)	0.208(4)	0.05						
H(5)	0.060(4)	0.774(6)	0.3417(18)	0.05						
H(6)	0.150(2)	0.659(5)	0.444(5)	0.05						

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN LEGRANDITE

As(1)-O(1)a	1.676(2)	As(2)-O(5)b	1.698(2)
As(1)-O(2)	1.690(2)	As(2)-O(6)	1.679(2)
As(1)-O(3)	1.692(2)	As(2)-O(7)	1.667(2)
As(1)-O(4)a	1.689(2)	As(2)-O(8)	1.689(2)
<As(1)-O>	1.687	<As(2)-O>	1.683
Zn(1)-O(1)a	2.042(2)	Zn(2)-O(2)c	2.057(2)
Zn(1)-O(5)a	2.145(2)	Zn(2)-O(3)	2.045(2)
Zn(1)-O(6)c	2.145(2)	Zn(2)-O(6)c	1.963(2)
Zn(1)-O(7)	2.101(2)	Zn(2)-O(7)	2.128(2)
Zn(1)-O(10)c	2.100(2)	Zn(2)-O(11)	1.965(2)
Zn(1)-O(10)b	2.133(2)	<Zn(2)-O>	2.032
<Zn(1)-O>	2.111		
Zn(3)-O(1)	2.346(2)	Zn(4)-O(2)c	2.012(2)
Zn(3)-O(5)	2.012(2)	Zn(4)-O(3)	2.113(2)
Zn(3)-O(8)	1.972(2)	Zn(4)-O(4)e	2.011(2)
Zn(3)-O(10)	2.096(2)	Zn(4)-O(9)e	2.071(2)
Zn(3)-O(11)d	1.963(2)	Zn(4)-O(12)f	2.011(2)
<Zn(3)-O>	2.078	<Zn(4)-O>	2.044
O(11)-H(2)	0.980(1)	O(10)-H(1)	0.980(1)
H(2)....O(8)	1.93(3)	H(1)....O(8)	2.86(3)
O(11)-H(2)-O(8)	145(4)	O(10)-H(1)-O(8)	130(4)
O(12)-H(5)	0.980(1)	O(9)-H(3)	0.980(1)
O(12)-H(6)	0.980(1)	O(9)-H(4)	0.980(1)
H(5)....O(4)	1.77(2)	H(3)....O(8)	2.078(8)
H(6)....O(11)	1.666(12)	H(4)....O(4)e	1.83(2)
O(12)-H(5)-O(4)	156(4)	O(11)-H(2)-O(8)	171(4)
O(12)-H(6)-O(11)	165(4)	O(11)-H(2)-O(8)	152(4)

a: x, y-1, z; b: -x+1, y-½, -z+½; c: x, -y+½, z+½; d: x, -y+¾, z-½; e: -x, y-½, -z+½; f: -x, -y+1, -z+1.

TABLE 4. BOND-VALENCE TABLE FOR LEGRANDITE*

	As(1)	As(2)	Zn(1)	Zn(2)	Zn(3)	Zn(4)	Σ'	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	Σ
O(1)	1.279		0.401		0.176		1.856							1.856
O(2)	1.231			0.385		0.435	2.051							2.051
O(3)	1.225			0.398		0.331	1.954							1.954
O(4)	1.235					0.436	1.671				0.17	0.19		2.031
O(5)		1.205	0.304		0.435		1.944							1.944
O(6)		1.268	0.304	0.497			2.069							2.069
O(7)		1.310	0.342	0.318			1.970							1.970
O(8)		1.235			0.485		1.720	0.02	0.15	0.12				2.030
O(9)						0.374	0.374			0.88	0.83			2.084
O(10)			0.343		0.347		1.004	0.98						1.984
			0.314											
O(11)				0.494	0.497		0.991		0.85				0.25	2.091
O(12)						0.436	0.436					0.81	0.75	1.996
Σ	4.970	5.028	2.008	2.092	1.940	2.012		1.00	1.00	1.00	1.00	1.00	1.00	

* calculated using the parameters of Brown & Altermatt (1985).

Perspex discs, ground, polished, carbon-coated, and analyzed with a Cameca SX-100 electron microprobe operating under the following conditions in wavelength-dispersion mode: excitation voltage: 15 kV, specimen current: 10 nA, beam size: 10 μm , peak count-time: 20 s, background count-time: 20 s. We used the following standards and crystals for $K\alpha$ X-ray lines: Zn, As: adamite; Fe: fayalite; Mn: spessartine; Cu was sought but not detected. Chemical formulae were calculated on the basis of six anions with one (OH) group and one (H_2O) group. The chemical compositions and unit formulae are given in Table 5.

Infrared spectroscopy

The FTIR spectrum was collected using a Bruker Tensor 27 FTIR spectrometer equipped with a KBr beam splitter and a DLATGS detector. The spectrum over the range 4000–400 cm^{-1} was obtained by averaging 100 scans with a resolution of 4 cm^{-1} . Base-line correction was done using the OPUS spectroscopic software (Bruker Optic GmbH). The spectrum is shown in Figure 1.

DESCRIPTION OF THE STRUCTURE

Cation polyhedra

Each cation polyhedron is labeled by its central cation site. There are two distinct As sites, each occupied by As^{5+} , as indicated by the site scattering, and tetrahedrally coordinated by O anions with $\langle\text{As}-\text{O}\rangle$

distances of 1.687 and 1.683 Å, close to values previously reported for $\langle\text{As}^{5+}-\text{O}\rangle$ distances, *e.g.*, 1.680 in scorodite (Hawthorne 1976a), 1.681 Å in adamite (Hawthorne 1976b), and 1.685 Å in brandtite (Herwig & Hawthorne 2006). There are four distinct Zn sites, all of which are occupied by Zn, as indicated by the site scattering at each site. Zn(1) is octahedrally coordinated by O anions with a $\langle\text{Zn}-\text{O}\rangle$ distance of 2.111 Å. Zn(2), Zn(3) and Zn(4) are [5]-coordinated by O anions with $\langle\text{Zn}-\text{O}\rangle$ distances of 2.032, 2.078 and 2.044 Å.

Bond topology

The polyhedron linkage is quite complicated in legrandite, as is commonly the case in minerals in which

TABLE 5. CHEMICAL COMPOSITION (wt.%) AND UNIT-CELL CONTENT (*apfu*)

	Colorless	Pale blue		Colorless	Pale blue
As_2O_5	37.73	37.16	As	1.004	1.005
ZnO	52.51	51.50			
FeO	0.10	0.24	Zn	1.973	1.967
MnO	0.28	0.22	Mn^{2+}	0.012	0.010
H_2O	<u>8.84</u>	<u>8.69</u>	Fe^{2+}	<u>0.004</u>	<u>0.010</u>
Sum	99.46	97.81	Sum	1.989	1.987
			OH	1	1
			H_2O	1	1

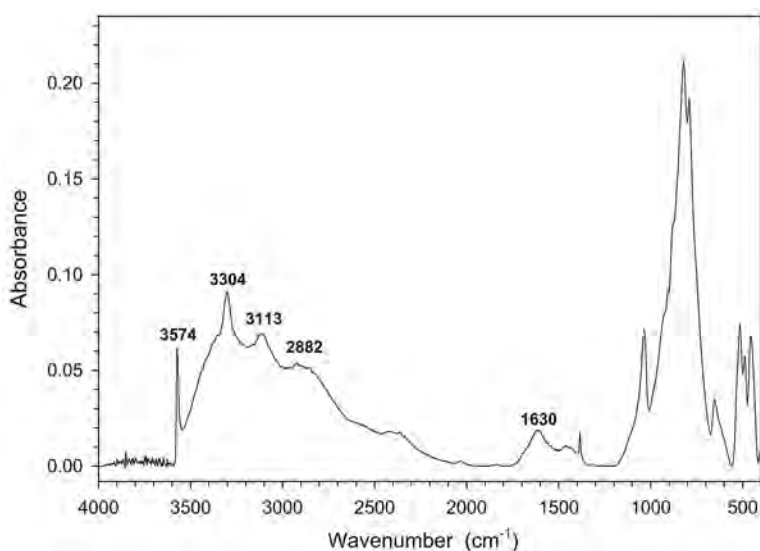


FIG. 1. The infrared spectrum of legrandite.

the divalent cations are five-coordinated. Two Zn(1) octahedra share an edge (Fig. 2) and the vertices *cis* to this edge are linked by As(2) tetrahedra, forming an $[M_2\Phi_6(TO_4)_2]$ cluster (Φ is an unspecified anion) that Hawthorne (1983) showed is one of the four clusters of two octahedra and two tetrahedra that show optimum agreement with the valence-sum rule. This cluster links to other clusters of the same sort by sharing vertices between octahedra and tetrahedra to form a sheet (Fig. 3a) with alternate chains of clusters tilted in opposite directions (Fig. 3b).

The Zn(2) and Zn(4) polyhedra share an edge to form a dimer, and the dimer shares a corner with the Zn(3) polyhedron to form a trimer (Fig. 4), and these trimers form a disconnected layer parallel to (100) (Fig. 4). This layer is quite corrugated (Fig. 5a), and two of these layers, facing in opposite directions, sandwich the Zn(1)–As(2) layer (Fig. 3) as shown in Figure 5b. The result is a very thick layer (Fig. 5b) parallel to (100), with Zn(4) polyhedra projecting from both sides of the sheet. These sheets stack in the *a* direction such that the projecting Zn(4) polyhedra fit into the staggered gaps in the opposing layer (Fig. 6). The layers are linked in the *a* direction by As(1) tetrahedra (Fig. 6a) and hydrogen bonding (Fig. 6b).

Interstitial hydrogen-bond arrangements

The stereochemical details of the hydrogen bonding are given in Table 3. There are two (OH) groups [O(10) and O(11)] and two (H₂O) groups [O(9) and O(12)]. The environment of the two (OH) groups is shown in Figure 7. Both H(1) and H(2) project into a cavity enclosed by the Zn(1), Zn(2), and Zn(3) polyhedra.

The H(1) atom is 2.86 Å from the O(8) anion; is this a hydrogen bond? Brown (1976) has examined hydrogen bonding in a series of perchloric-acid hydrates: H(ClO₄)

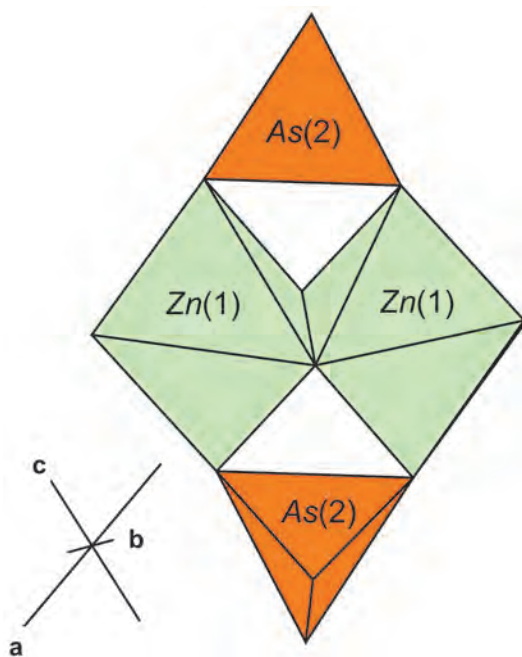


FIG. 2. The $[M_2\Phi_6(TO_4)_2]$ cluster (Φ is an unspecified anion) in legrandite; Zn(1) octahedra are pale green, As(2) tetrahedra are orange.

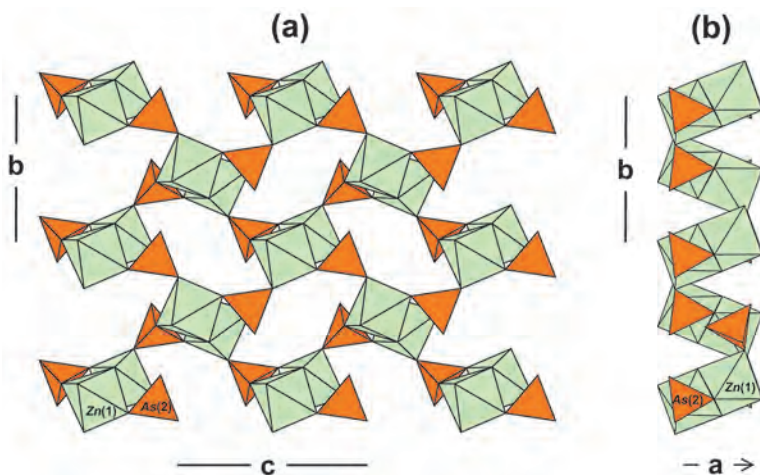


FIG. 3. The $[M_2\Phi_6(TO_4)_2]$ clusters in legrandite, linked by sharing of vertices between Zn octahedra and As tetrahedra to form a sheet; (a) projected onto (100); (b) viewed parallel to the plane of the sheet. Legend as in Figure 2.

FIG. 4. The disconnected layer of trimers of Zn polyhedra in legrandite: Zn(2) and Zn(4) are yellow, Zn(3) is mauve.

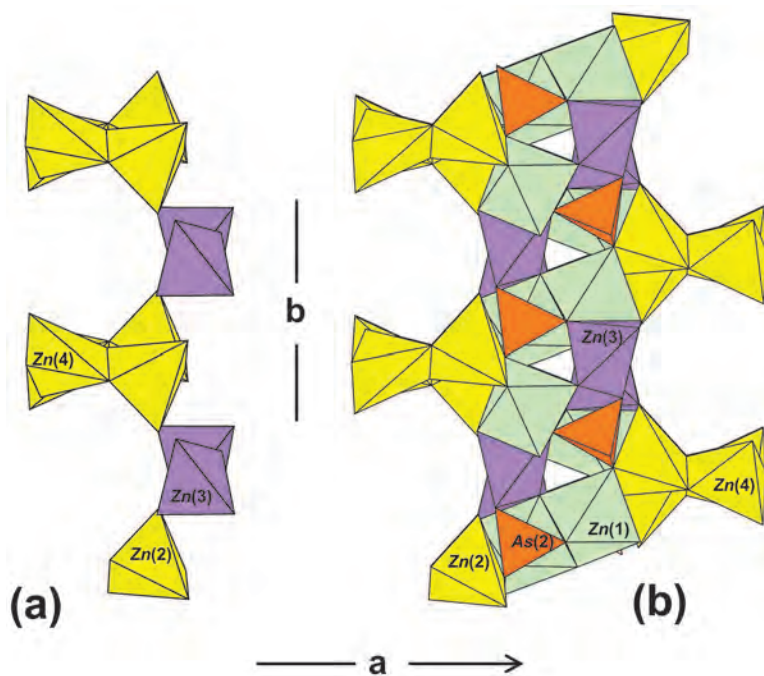
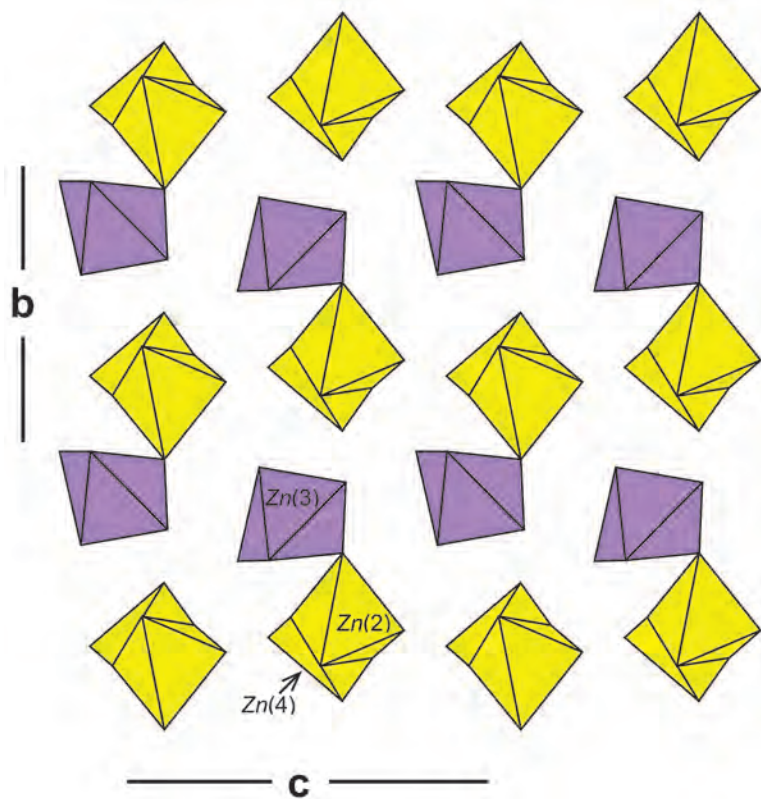


FIG. 5. The intercalation of layers of polyhedra in legrandite projected onto (001); (a) the disconnected layer of trimers of Zn octahedra viewed edge-on; (b) the layer of $[M_2\Phi_6(TO_4)_2]$ clusters intercalated between two layers of Zn trimers. Legend as in Figures 2 and 4.

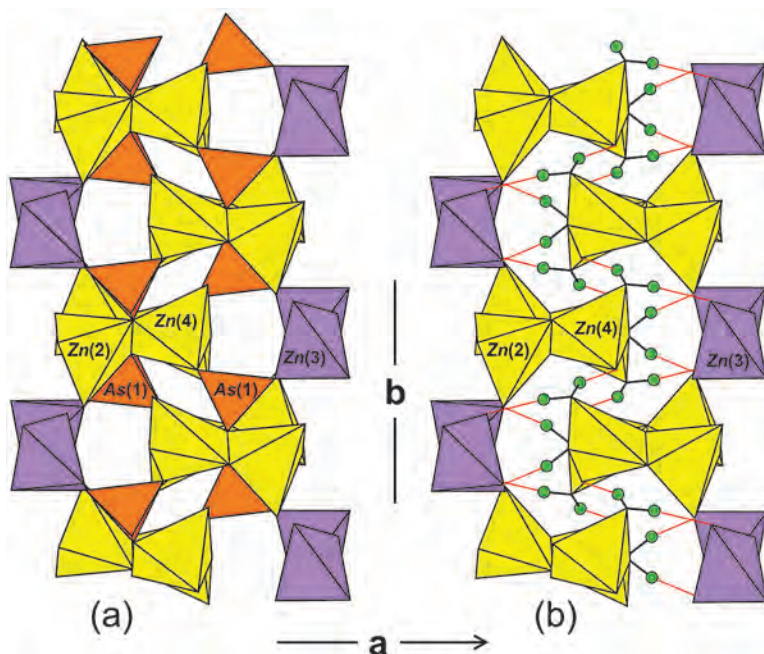


FIG. 6. (a) The Zn-As framework, omitting Zn(1) octahedra, in legrandite; (b) the corresponding Zn framework, showing the overall pattern of hydrogen bonds. Legends as in Figures 2 and 4, plus H atoms as green circles, O(donor)-H bonds as black lines, and hydrogen bonds as thin red lines.

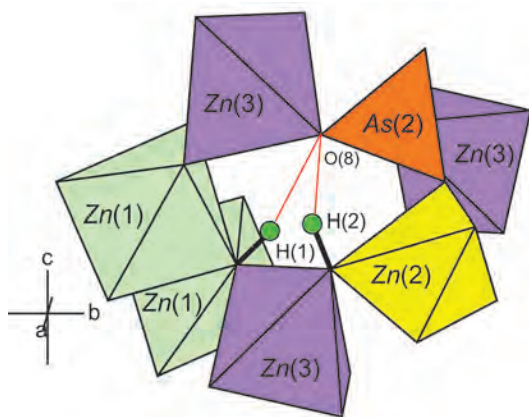


FIG. 7. Details of the O(donor), H and O(acceptor) atoms and associated hydrogen bonds for the (OH) groups in legrandite. Legend as in Figure 6.

(H₂O)_n ($n = 1, 2, 2.5, 3, 3.5$). These compounds are of particular interest as the perchlorate groups are held together only by hydrogen bonds. Brown (1976) used the valence-sum rule to show that hydrogen separations

up to 3.1 Å are significant hydrogen bonds. Thus the H(1)...O(8) distance of 2.86 Å constitutes a hydrogen bond, even though it is significantly longer than the other hydrogen bonds in the legrandite structure. The H(2) atom is 1.93 Å from the O(8) anion (Table 3), indicating a much stronger hydrogen bond than that involving H(1).

Figure 6a shows the part of the structure where the sheets in Figure 5b join together. The environment of the two (H₂O) groups is shown in Figure 6b, the same part of the structure as that shown in Figure 6a, but with the arsenate groups removed for clarity. The (H₂O) groups attach to the Zn(4) polyhedron and form a convoluted sheet (seen end-on in Fig. 6b) through the structure. The detailed stereochemistry around the two (H₂O) groups is shown in Figure 8. The H-O(acceptor) distances are all in the most common range for hydrogen bonds (1.65–2.08 Å) and the O(donor)-H...O(acceptor) angles are all close to 165°.

Hydrogen bonding and the infrared spectrum

Inspection of the H...O bond-lengths (Table 3) shows that they vary in the range 1.66–2.86 Å. It is well-known (e.g., Libowitzky 1999) that the principal O-H stretching frequency in the infrared is strongly corre-

lated with the H...O distance in inorganic materials, and the wide range in H...O bond-lengths in legrandite should be reflected in its infrared spectrum. Inspection of Figure 1 shows this to be the case: the principal bands show absorption frequencies from 3574 to 2882 cm^{-1} . The bands from (OH) groups are generally much narrower than bands from (H_2O) groups, and broaden with decreasing absorption frequency (e.g., Groat *et al.* 1995). This allows us to assign the bands as follows: 3574 cm^{-1} : O(10)–H(1); 3304 cm^{-1} : O(11)–H(2); 3113 cm^{-1} : O(9) (H_2O); 2882 cm^{-1} : O(12) (H_2O). As shown in Figure 9, this assignment produces reasonable accord with the relation of Libowitzky (1999).

A note on the color of legrandite

Legrandite is normally bright yellow. However, the legrandite (from the Tsumeb mine) used in this work

is colorless to pale blue. Initially, we suspected the presence of minor Cu, but chemical analysis (Table 5) showed this not to be the case: we could not detect Cu in either sample. Inspection of the formulae (Table 5) shows a slightly higher Fe content in the pale blue crystals, and this is presumably the origin of the pale blue color.

ACKNOWLEDGEMENTS

We thank Mark Cooper for his help with the experimental part of this work, and Bill Pinch for suggesting we look at this curiously pale-blue mineral. This work was supported by a Canada Research Chair in Crystallography and Mineralogy, Research Tools and Equipment, Major Facilities Access and Discovery Grants from the Natural Sciences and Engineering Research Council of Canada and Canada Foundation for Innovation Grants to FCH.

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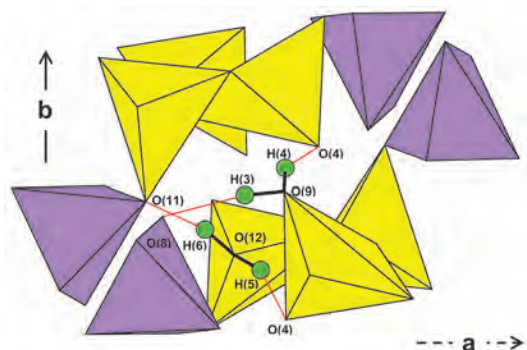


FIG. 8. Details of the O(donor), H and O(acceptor) atoms and associated hydrogen bonds for the (H_2O) groups in legrandite. Legend as in Figure 6; the view is rotated slightly away from (001) to minimize overlap.

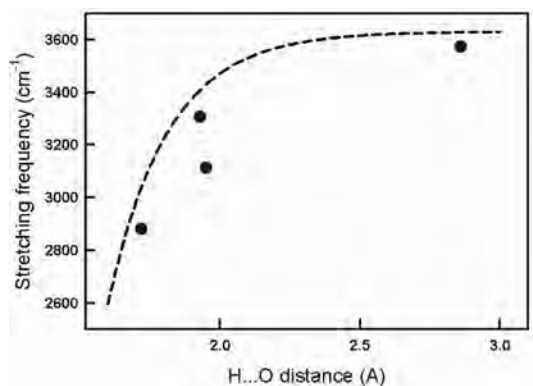


FIG. 9. Variation in principal OH-stretching frequency as a function of hydrogen bond length in legrandite; the curve is the relation of Libowitzky (1999).

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Received May 27, 2012, revised manuscript accepted January 25, 2013.

