

# Ianbruceite, ideally $[\text{Zn}_2(\text{OH})(\text{H}_2\text{O})(\text{AsO}_4)](\text{H}_2\text{O})_2$ , a new arsenate mineral from the Tsumeb mine, Otjikoto (Oshikoto) region, Namibia: description and crystal structure

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## ABSTRACT

Ianbruceite, ideally  $[\text{Zn}_2(\text{OH})(\text{H}_2\text{O})(\text{AsO}_4)](\text{H}_2\text{O})_2$ , is a new supergene mineral from the Tsumeb mine, Otjikoto (Oshikoto) region, Namibia. It occurs as thin platy crystals up to 80  $\mu\text{m}$  long and a few  $\mu\text{m}$  thick, which form flattened aggregates up to 0.10 mm across, and ellipsoidal aggregates up to 0.5 mm across. It is associated with coarse white leiteite, dark blue köttigite, minor legrandite and adamite. Ianbruceite is sky blue to very pale blue with a white streak and a vitreous lustre; it does not fluoresce under ultraviolet light. It has perfect cleavage parallel to (100), is flexible, and deforms plastically. The Mohs hardness is 1 and the calculated density is 3.197  $\text{g cm}^{-3}$ . The refractive indices are  $\alpha = 1.601$ ,  $\beta = 1.660$ ,  $\gamma = 1.662$ , all  $\pm 0.002$ ;  $2V_{\text{obs}} = 18(2)^\circ$ ,  $2V_{\text{calc}} = 20^\circ$ , and the dispersion is  $r < v$ , weak. Ianbruceite is monoclinic, space group  $P2_1/c$ ,  $a = 11.793(2)$ ,  $b = 9.1138(14)$ ,  $c = 6.8265(10)$  Å,  $\beta = 103.859(9)^\circ$ ,  $V = 712.3(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $a:b:c = 1.2940:1:0.7490$ . The seven strongest lines in the X-ray powder diffraction pattern [ $d$  (Å),  $I$ , ( $hkl$ )] are as follows: 11.29, 100, (100); 2.922, 17, (130); 3.143, 15, ( $\bar{2}02$ ); 3.744, 11, (300); 2.655, 9, (230); 1.598, 8, ( $\bar{1}52$ ); 2.252, 7, (222). Chemical analysis by electron microprobe gave  $\text{As}_2\text{O}_5$  36.27,  $\text{As}_2\text{O}_3$  1.26,  $\text{Al}_2\text{O}_3$  0.37,  $\text{ZnO}$  49.72,  $\text{MnO}$  0.32,  $\text{FeO}$  0.71,  $\text{K}_2\text{O}$  0.25,  $\text{H}_2\text{O}_{\text{calc}}$  19.89, sum 108.79 wt.%; the very high oxide sum is due to the fact that the calculated  $\text{H}_2\text{O}$  content is determined from crystal-structure analysis, but  $\text{H}_2\text{O}$  is lost under vacuum in the electron microprobe.

The crystal structure of ianbruceite was solved by direct methods and refined to an  $R_1$  index of 8.6%. The As is tetrahedrally coordinated by four O anions with a mean As–O distance of 1.687 Å. Zigzag [ $^{51}\text{Zn}^{61}\text{Zn}\phi_7$ ] chains extend in the **c** direction and are linked in the **b** direction by sharing corners with  $(\text{AsO}_4)$  tetrahedra to form slabs with a composition  $[\text{Zn}_2(\text{OH})(\text{H}_2\text{O})(\text{AsO}_4)]$ . The space between these slabs is filled with disordered  $(\text{H}_2\text{O})$  groups and minor lone-pair stereoactive  $\text{As}^{3+}$ . The ideal formula derived from chemical analysis and crystal-structure solution and refinement is  $[\text{Zn}_2(\text{OH})(\text{H}_2\text{O})(\text{AsO}_4)](\text{H}_2\text{O})_2$ .

**KEYWORDS:** ianbruceite, new mineral species, arsenate, Tsumeb mine, Otjikoto (Oshikoto) region, Namibia, crystal structure, electron microprobe analysis, optical properties.

## Introduction

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THE Tsumeb mine in the Otjikoto (Oshikoto) region of Namibia is famous for the diversity and

spectacular appearance of its minerals (Pinch and Wilson, 1977), and was a major source of Cu-Pb-Zn ores for most of the twentieth century. A pipe-like structure of ‘pseudoapelite’ (Weber and Wilson, 1977) intrudes a sequence of arkoses, greywackes and dolomitic limestones; pods, lenses and veins of sulfide occur at the periphery of the pipe in a matrix of disseminated ore. Extensive oxidation zones were encountered between the surface and 300 m and from ~800–1450 m where a fracture zone intersects the orebody (Weber and Wilson, 1977). A wide variety of secondary minerals (Pinch and Wilson, 1977) and exotic parageneses (Keller, 1977) have been described and new species continue to be discovered.

Ianbruceite was characterized independently by researchers at the University of Manitoba and the Royal Ontario Museum, Canada, and the University of Hamburg, Germany. Data from both groups were combined at a late stage and are presented here. In 1994, one of the authors (GG) received a specimen of leiteite, overgrown by dark blue crystals of köttigite and pale blue crystals of an unknown phase, from the ‘Zinc Pocket’ on the 44 level of Tsumeb mine. It was described as a probable new species, using the code GS17, and figured in Gebhard (1999: p. 296). Investigations of a specimen of GS17 in the mineral collection of the Royal Ontario Museum independently identified a new hydroxy-hydrated zinc arsenate. It is named ianbruceite for Ian Bruce (born 01/04/1969 at Okehampton, Devon, England), a prime mover in the recent reopening the Tsumeb mine for mineral collecting, who has made significant contributions to the mineral collections of many of the world’s major museums through his professional activities. The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2011-49). The holotype specimen of ianbruceite is registered in the mineral collection of the Department of Natural History, Royal Ontario Museum (catalogue number M53150) and holotype crystals are deposited in the collection of the Mineralogical Museum of the University of Hamburg, Grindelallee 48, D-20146 Hamburg, Germany (catalogue number TS 119B).

### Physical properties

Ianbruceite occurs as aggregates of thin flakes and tapered platy crystals up to 80  $\mu\text{m}$  long and a

few  $\mu\text{m}$  thick, and as rounded ellipsoidal aggregates up to 0.5 mm across. It is associated with coarse white leiteite, dark blue köttigite, minor legrandite and adamite (Fig. 1). The crystal forms are as follows: {100} dominant, {011} and {0 $\bar{5}$ 1} prominent. It is sky blue to very pale blue with a white streak and a vitreous lustre, and does not fluoresce under ultraviolet light. The platy crystals have perfect cleavage parallel to (100); no parting or twinning was observed. The Mohs hardness is 1. Ianbruceite is flexible and does not fracture but deforms plastically. The calculated density is 3.197 g cm<sup>-3</sup>. Optical properties were measured using a Bloss spindle stage at a wavelength of 590 nm (using a gel filter). The indices of refraction are  $\alpha = 1.601$ ,  $\beta = 1.660$ ,  $\gamma = 1.662$ , all  $\pm 0.002$ ;  $2V_{\text{obs}} = 18(2)^\circ$ ,  $2V_{\text{calc}} = 20^\circ$ , and the dispersion is  $r < v$ , weak. No pleochroism was observed in the (100) plane, and the orientation is as follows:  $X \wedge a = 12.0^\circ$  (in  $\beta$  obtuse),  $Y \parallel b$ ,  $Z \wedge c = 4.7^\circ$  (in  $\beta$  obtuse).

### Raman spectroscopy

Spectra were collected in back-scattered mode on a HORIBA Jobin Yvon-LabRAM ARAMIS integrated confocal micro-Raman system equipped with a 460 mm focal length spectrograph and a multichannel air-cooled ( $-70^\circ\text{C}$ )

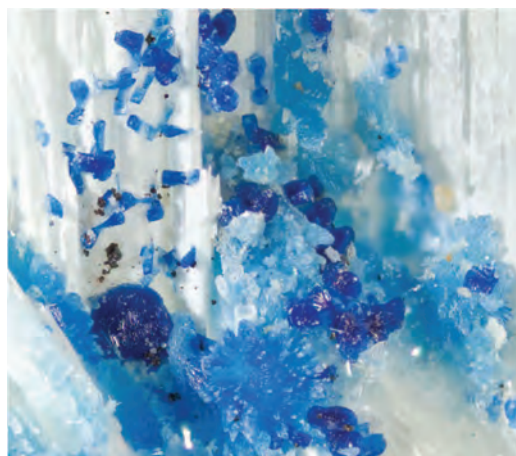


FIG. 1. Sky blue to blue crystal aggregates of platy, tapered ianbruceite crystals with blue to deep blue copper-bearing aggregates of köttigite on white leiteite from the Tsumeb mine, Tsumeb, Namibia. Width of the image is 1.3 mm. Photo: K.-C. Lyncker, Hamburg.

## IANBRUCEITE, A NEW SUPERGENE MINERAL FROM TSUMEB

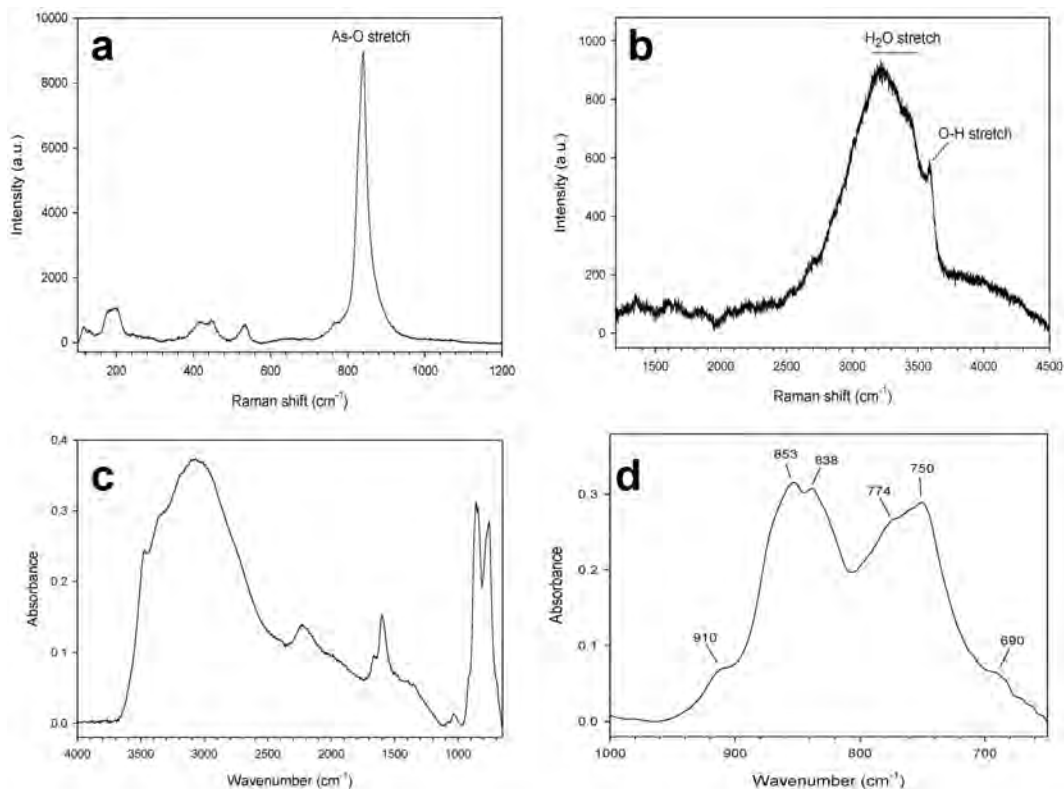


FIG. 2. (a,b) The Raman spectrum of ianbruceite; (c,d) the infrared spectrum of ianbruceite.

TABLE 1. Chemical composition of ianbruceite.

Constituent	Mean (wt.%) <sup>1</sup>	Range <sup>1</sup>	Mean (wt.%) <sup>2</sup>	Range <sup>2</sup>
As <sub>2</sub> O <sub>5</sub>	36.27(1.07)	35.71–39.54	36.48	30.78–42.20
As <sub>2</sub> O <sub>3</sub>	1.26			
Al <sub>2</sub> O <sub>3</sub>	0.37(19)	0.17–0.90	–	–
ZnO	49.72(92)	48.28–51.52	49.15	48.23–50.30
MnO	0.32(15)	0.16–0.57	–	–
FeO	0.71(18)	0.53–1.05	–	–
CaO	–	–	0.06	0.02–0.11
K <sub>2</sub> O	0.25(4)	0.19–0.30	–	–
H <sub>2</sub> O <sub>calc</sub>	19.89 <sup>3</sup>		14.31 <sup>4</sup>	–
Total	108.79		100.00	

Elements that were sought but not detected: Cu, Na, Ca, Si, P, S, Mg, Ti, V, Cr, Ni, F, Cl.

<sup>1</sup> Data gathered on a Cameca SX100 instrument at 15 kV, 10 nA, with a 5 μm beam diameter, mean of 10 determinations.

<sup>2</sup> Data gathered on a Cameca SX100 instrument at 15 kV, 20 nA, with an ~1 μm beam diameter.

<sup>3</sup> The H<sub>2</sub>O value calculated from structure refinement.

<sup>4</sup> The H<sub>2</sub>O value calculated by difference.

CCD detector. A magnification of  $100\times$  was used with an estimated spot size of  $1\ \mu\text{m}$ , a  $1800\ \text{lines}\ \text{mm}^{-1}$  grating, an excitation radiation of  $532\ \text{nm}$ , and a laser power between  $5$  and  $12.5\ \text{mW}$ . The spectrometer was calibrated using the  $520.7\ \text{cm}^{-1}$  line of silicon. The Raman spectrum is shown in Fig. 2*a,b*. In the  $100$ – $1200\ \text{cm}^{-1}$  region, there is a prominent peak at  $840\ \text{cm}^{-1}$  that is assigned to  $\text{As}^{5+}$ –O stretching vibrations. Peaks at  $534$ ,  $448$  and  $420\ \text{cm}^{-1}$  are assigned to Zn–O stretching and bending vibrations of the  $(\text{AsO}_4)$  groups; the  $192\ \text{cm}^{-1}$  peak is a lattice mode. In the  $2500$ – $4000\ \text{cm}^{-1}$  region, there is a broad envelope centred on  $3224\ \text{cm}^{-1}$  and weak shoulders at  $3441$  and  $3224\ \text{cm}^{-1}$  that are produced by  $\text{H}_2\text{O}$  stretching vibrations. The sharp peak at  $3600\ \text{cm}^{-1}$  is an O–H stretch.

The first Raman spectrum of ianbruceite that was collected had peaks due to C–H stretching; the specimen had been immersed in alcohol and contamination was suspected. This proved to be the case as the Raman spectra of grains of ianbruceite that had not been immersed in alcohol did not have C–H stretches (Fig. 2). This suggests that the interstitial space in the structure that is occupied by disordered  $(\text{H}_2\text{O})$  groups can absorb alcohol.

### Infrared spectroscopy

The Fourier transform infrared (FTIR) spectra were collected using a Bruker Hyperion 2000 IR microscope equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride detector. Spectra in the range  $4000$ – $650\ \text{cm}^{-1}$  were obtained by averaging 100 scans with a resolution of  $4\ \text{cm}^{-1}$ . A very broad envelope centred at  $\sim 3000\ \text{cm}^{-1}$  and sharp peaks at  $\sim 1600$  and  $\sim 1670\ \text{cm}^{-1}$  (Fig. 2*c*), are indicative of  $\text{H}_2\text{O}$  stretches and H–O–H bends, and indicate the presence of considerable  $\text{H}_2\text{O}$  in ianbruceite. Fine structure in the broad envelope, particularly in the region around  $3500\ \text{cm}^{-1}$ , is indicative of the presence of (OH), which is in accord with the crystal structure refinement. The strong peaks at  $853$ ,  $838$ ,  $774$  and  $750\ \text{cm}^{-1}$  (Fig. 2*d*) are assigned to  $\text{As}^{5+}$ –O stretching vibrations, the weak shoulder at  $\sim 690\ \text{cm}^{-1}$  is assigned to an  $\text{As}^{3+}$ –O stretching vibration, and the weak shoulder at  $\sim 930\ \text{cm}^{-1}$  to an  $\text{As}^{3+}$ –O–H bending vibration. The low intensity of the peaks involving  $\text{As}^{3+}$  are in accord with the very low occupancy ( $\sim 0.04$ ) of the sites containing  $\text{As}^{3+}$ .

### Chemical composition

Crystals were analysed on two Cameca SX-100 electron microprobes operating in wavelength-dispersive mode in the conditions listed in Table 1. The data were reduced and corrected by the PAP method of Pouchou and Pichoir (1985) and the ZAF method. Raman spectra (Fig. 2) show a broad intense band in the region  $2500$ – $4000\ \text{cm}^{-1}$ , which is indicative of  $(\text{H}_2\text{O})$ , and a sharp peak at  $3600\ \text{cm}^{-1}$  indicative of (OH). The quantity of (OH) and  $(\text{H}_2\text{O})$  groups in

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

$I_{\text{obs}}$	$I_{\text{calc}}^*$	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}^*$ (Å)	$h$	$k$	$l$
100	100	11.29	11.290	1	0	0
2	1	4.549	4.571	0	2	0
11	9	3.744	3.764	3	0	0
	<1		3.759	0	2	1
	<1		3.718	$\bar{1}$	2	1
15	25	3.143	3.194	$\bar{2}$	0	2
	<1		3.179	$\bar{1}$	1	2
	<1		3.106	0	1	2
	2		3.016	$\bar{2}$	1	2
	1		2.987	1	0	2
17	14	2.922	2.942	1	3	0
7	7	2.819	2.839	1	1	2
	<1		2.823	4	0	0
9	17	2.655	2.682	2	3	0
	<1		2.618	$\bar{2}$	2	2
1	4	2.480	2.501	1	2	2
5	9	2.381	2.407	$\bar{3}$	2	2
	<1		2.368	3	3	0
	<1		2.363	$\bar{4}$	1	2
7	6	2.252	2.259	2	2	2
	<1		2.258	5	0	0
	<1		2.240	1	4	0
	2		2.054	$\bar{5}$	1	2
2	3	1.890	1.895	$\bar{1}$	4	2
	<1		1.892	4	1	2
2	3	1.804	1.817	$\bar{1}$	3	3
	<1		1.815	1	4	2
	<1		1.814	5	3	0
4	4	1.692	1.698	$\bar{6}$	2	2
	<1		1.695	$\bar{2}$	0	4
	<1		1.691	$\bar{1}$	0	4
	1		1.649	0	0	4
8	9	1.598	1.609	$\bar{1}$	5	2
	<1		1.601	6	3	0
	<1		1.600	0	5	2
	<1		1.597	$\bar{4}$	0	4

\* Calculated from the refined crystal structure.

TABLE 3. Miscellaneous information for ianbruceite structure solutions and refinements.

Parameter	Refinement 1 (Univ. of Manitoba)	Refinement 2 (Univ. of Hamburg)
<i>a</i> (Å)	11.793(2)	11.612(7)
<i>b</i>	9.1138(14)	9.142(5)
<i>c</i>	6.8265(10)	6.793(3)
$\beta$ (°)	103.859(9)	103.52(4)
<i>V</i> (Å <sup>3</sup> )	712.3(3)	701.1(7)
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>Z</i>	4	4
Crystal size (µm)	40 × 40 × 4	60 × 50 × 8
Radiation	MoK $\alpha$	MoK $\alpha$
No. of reflections	10,229	6337
No. unique reflections	1352	1381
<i>R</i> <sub>merge</sub> (%)	3.51	9.9
<i>R</i> <sub>obs</sub> (%)	8.6	12.4

ianbruceite was determined by crystal-structure refinement and the resultant composition is listed in Table 1 (column 2).

In ianbruceite, there are well-ordered (OH) and (H<sub>2</sub>O) groups that are associated with the *Zn* sites of the [Zn<sub>2</sub>(OH)(H<sub>2</sub>O)(AsO<sub>4</sub>)] structural unit. There are also two interstitial (H<sub>2</sub>O) groups with a large degree of positional disorder (i.e. large anisotropic-displacement parameters). Some additional (minor) electron density was identified in the difference-Fourier map ~1.7 Å from the (OH) group at O(4); we interpret this as belonging to As<sup>3+</sup> as part of an [As<sup>3+</sup>(OH)<sub>2</sub>O] group, with O(4) as the O ligand. Where the [As<sup>3+</sup>(OH)<sub>2</sub>O] group is present, one of the neighbouring interstitial (H<sub>2</sub>O) sites must be vacant (as As<sup>3+</sup>... (H<sub>2</sub>O) is <2 Å).

If we initially disregard any contribution from [As<sup>3+</sup>(OH)<sub>2</sub>O] and normalize the chemical formula to 8 anions [O<sub>4</sub> + (OH) + (H<sub>2</sub>O)<sub>3</sub>], there is a slight excess in the number of As<sup>3+</sup> cations. If we then include minor [As<sup>3+</sup>(OH)<sub>2</sub>O]<sub>*x*</sub> in the calculation (with *x* = 0.04), there is an improvement in stoichiometry. The net formula unit can be expressed in terms of the [As<sup>3+</sup>(OH)<sub>2</sub>O]<sub>*x*</sub> and [(OH)(H<sub>2</sub>O)]<sub>(1-*x*)</sub> contributions (where *x* = 0.04 for the crystal analysed by electron microprobe). The resulting anion part of the formula unit contains O<sub>4.04</sub> + (OH)<sub>1.04</sub> + (H<sub>2</sub>O)<sub>2.96</sub> = 8.04 anions, and the chemical composition normalized accordingly gives the empirical formula K<sub>0.02</sub>(Zn<sub>1.93</sub>Fe<sub>0.03</sub>Al<sub>0.02</sub>Mn<sub>0.01</sub>)<sub>Σ=1.99</sub>(OH)<sub>0.96</sub>(H<sub>2</sub>O)(As<sup>3+</sup>O<sub>4</sub>)<sub>1</sub>[As<sup>3+</sup>(OH)<sub>2</sub>O]<sub>0.04</sub>(H<sub>2</sub>O)<sub>1.96</sub>. The idealized formula is [Zn<sub>2</sub>(OH)(H<sub>2</sub>O)(AsO<sub>4</sub>)](H<sub>2</sub>O)<sub>2</sub>. The (H<sub>2</sub>O) at the end of the formula is interstitial;

this has significant implications from a structural viewpoint, which are discussed below.

The interstitial (H<sub>2</sub>O) in ianbruceite is not held strongly in the structure. The crystal grains fracture extensively when exposed to the electron beam in vacuum in an electron microprobe. A comparison of the sum of the oxides and the calculated H<sub>2</sub>O content shows that considerable H<sub>2</sub>O is lost in this process. The loss of H<sub>2</sub>O results in anomalously high values for the remaining constituents, giving a high sum for the total oxides (Table 2). The weakly bonded nature of the interstitial (H<sub>2</sub>O) is apparent from two further observations. The interstitial space between the [Zn<sub>2</sub>(OH)(H<sub>2</sub>O)(AsO<sub>4</sub>)] slabs can absorb alcohol, as indicated by the Raman spectra, and preparation of material for powder diffraction resulted in a loss of interstitial (H<sub>2</sub>O), which is apparent if the *a* dimension derived from the single-crystal diffraction study (11.793 Å) and that derived from the powder diffraction study (11.583 Å) are compared.

### X-ray powder diffraction

Powder-diffraction data are listed in Table 2. The measured data were collected by the Hamburg group on a Nonius kappa CCD four-circle diffractometer in a Gandolfi-type arrangement using MoK $\alpha$  radiation and the *POWDERIZE* program. The calculated data were determined using *JANA2000* (Petříček and Dušek, 2000) from the single-crystal structure refinement.

Additional powder-diffraction data were collected by the Manitoba-Toronto group using



a 114.6 mm diameter Gandolfi camera. The film was digitized using an optical scanner that was calibrated for intensity and peak position using an external Si standard, and the following unit-cell parameters were obtained by least-squares refinement:  $a = 11.583(3)$ ,  $b = 9.159(2)$ ,  $c = 6.816(3)$  Å,  $\beta = 103.3(1)^\circ$  and  $V = 703.7(3)$  Å<sup>3</sup>. Significant interstitial H<sub>2</sub>O was lost when this sample was prepared for analysis, and as a result these data are not listed.

### Crystal-structure solution and refinement

All of the diffraction patterns showed extreme streaking along  $a^*$ . Very small crystals were used to try to improve the data quality, and the crystal-to-detector distance was increased to 8 cm to help resolve the rather diffuse maxima within the streaks. A small crystal which produced a reasonably precise unit cell was eventually found. It was attached to a tapered glass fibre and mounted on a Bruker D8 three-circle diffractometer equipped with a rotating-anode generator (MoK $\alpha$  radiation), multilayer optics and an APEX-II detector. A total of 10,229 intensities (3233 within the Ewald sphere) were collected to  $60^\circ 2\theta$  using 40 s per  $0.3^\circ$  frame. Empirical absorption corrections (*SADABS*; Sheldrick, 2008) were applied and equivalent reflections were corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. The unit-cell dimensions were obtained by least-squares refinement of the positions of 4921 reflections with  $I > 10\sigma I$  and are given in Table 3, together with other information pertaining to data collection and structure refinement.

All calculations were done with the *SHELXTL PC* (Plus) system of programs;  $R$  indices are of the form given in Table 3 and are expressed as percentages. 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 by direct methods and refined to convergence by full-matrix least-squares techniques with anisotropic-displacement parameters on all atoms. At this stage, difference-Fourier maps showed diffuse electron density in the space ( $\sim 4.7$  Å wide) between adjacent layers in the structure. Close inspection showed two weak maxima  $\sim 1.7$  Å from the O(4) anion. The only constituent in the electron-microprobe analysis that could possibly occur this close to an O atom is As, and we included two additional

TABLE 4. Atom coordinates, occupancies and displacement parameters (Å<sup>2</sup>) for ianbruceite.

	$x/a$	$y/b$	$z/c$	Occupancy	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
As(1)	0.36080(16)	0.91756(16)	0.0952(2)	1	0.0380(13)	0.0106(8)	0.0089(8)	-0.0008(5)	0.0073(7)	0.0004(6)	0.0189(7)
As(2)	0.806(3)	0.777(3)	0.492(4)	0.048(8)							0.004(11)
As(3)	0.778(4)	0.686(5)	0.484(6)	0.031(8)							0.011(17)
Zn(1)	0.6179(2)	0.0413(2)	0.4016(3)	1	0.0398(16)	0.0120(10)	0.0129(10)	-0.0005(6)	0.0083(9)	0.0015(8)	0.0208(8)
Zn(2)	0.6059(2)	0.7591(2)	0.1490(3)	1	0.020(7)	0.0198(10)	0.0124(9)	-0.0051(6)	0.0093(9)	-0.0003(8)	0.0235(7)
O(1)	0.4319(11)	0.7571(11)	0.0969(16)	1	0.009(7)	0.015(5)	0.017(5)	0.001(4)	0.006(5)	0.004(4)	0.017(2)
O(2)= $[H_2O]$	0.7964(10)	0.0882(14)	0.5118(18)	1	0.009(7)	0.045(8)	0.030(6)	0.027(5)	-0.003(5)	-0.002(5)	0.030(3)
O(3)	0.2201(11)	0.8861(13)	0.081(2)	1	0.022(7)	0.020(6)	0.054(8)	-0.017(5)	0.011(6)	-0.002(5)	0.032(3)
O(4)=(OH)	0.6690(11)	0.8134(12)	0.4307(15)	1	0.048(8)	0.011(5)	0.016(5)	0.006(4)	0.011(5)	-0.002(5)	0.024(3)
O(5)	0.4267(11)	0.0110(11)	0.3102(15)	1	0.048(8)	0.012(5)	0.010(5)	-0.002(4)	0.007(5)	-0.000(5)	0.023(3)
O(6)	0.3725(11)	0.0130(12)	-0.1104(15)	1	0.038(8)	0.023(6)	0.007(4)	0.004(4)	0.006(5)	-0.002(5)	0.023(3)
O(7)=(H <sub>2</sub> O)	0.056(3)	0.987(3)	-0.203(6)	0.96(8)	0.10(3)	0.11(3)	0.24(4)	-0.03(3)	-0.08(2)	0.035(18)	0.17(2)
O(8)=(H <sub>2</sub> O)	0.913(4)	0.769(4)	0.585(8)	0.91(9)	0.11(3)	0.13(4)	0.25(6)	-0.00(3)	-0.05(3)	-0.04(2)	0.17(3)

## IANBRUCEITE, A NEW SUPERGENE MINERAL FROM TSUMEB

TABLE 5. Selected interatomic distances (Å) and angles (°) in ianbruceite.

<i>As</i> (1)–O(1)	1.685(10)	<i>Zn</i> (1)–O(1)f	2.053(10)	<i>Zn</i> (2)–O(1)	1.997(12)
<i>As</i> (1)–O(3)	1.664(13)	<i>Zn</i> (1)–O(2)	2.103(12)	<i>Zn</i> (2)–O(4)	1.952(11)
<i>As</i> (1)–O(5)a	1.714(10)	<i>Zn</i> (1)–O(4)b	2.159(11)	<i>Zn</i> (2)–O(4)e	1.934(10)
<i>As</i> (1)–O(6)a	<u>1.684(10)</u>	<i>Zn</i> (1)–O(5)	2.209(13)	<i>Zn</i> (2)–O(5)f	2.322(10)
< <i>As</i> (1)–O>	<b>1.687</b>	<i>Zn</i> (1)–O(5)c	2.207(10)	<i>Zn</i> (2)–O(6)g	<u>2.117(11)</u>
		<i>Zn</i> (1)–O(6)d	<u>2.078(10)</u>	< <i>Zn</i> (2)–O>	<b>2.064</b>
		< <i>Zn</i> (1)–O>	<b>2.135</b>		
Partially occupied <i>As</i> sites				Hydroxyl H-bond	
<i>As</i> (2)– <i>As</i> (3)	0.89(5)			O(4)···O(8)	2.84(4)
<i>As</i> (2)–O(4)	1.60(3)				
<i>As</i> (3)–O(4)	1.71(5)				
Structural (H <sub>2</sub> O)		Interstitial (H <sub>2</sub> O)		Interstitial (H <sub>2</sub> O)	
O(2)···O(3)h	2.784(17)	O(7)···O(3)	2.56(3)	O(8)···O(7)h	2.69(5)
O(2)···O(3)i	2.845(18)	O(7)···O(8)f	2.69(5)	O(8)···O(7)j	2.78(5)
O(3)h–O(2)–O(3)i	97.1(5)	or		O(7)h–O(8)–O(7)j	120.2(1.5)
		O(7)···O(8)k	2.78(5)		
		O(3)–O(7)–O(8)f	95.3(1.3)		
		or			
		O(3)–O(7)–O(8)k	113.1(1.5)		

Equivalent positions are as follows: a:  $x, y+1, z$ ; b:  $x, y-1, z$ ; c:  $\bar{x}+1, \bar{y}, \bar{z}+1$ ; d:  $\bar{x}+1, \bar{y}, \bar{z}$ ; e:  $x, \bar{y}+3/2, z-1/2$ ; f:  $\bar{x}+1, y+1/2, \bar{z}+1/2$ ; g:  $\bar{x}+1, \bar{y}+1, \bar{z}$ ; h:  $\bar{x}+1, y-1/2, \bar{z}+1/2$ ; i:  $\bar{x}+1, \bar{y}+1, \bar{z}+1$ ; j:  $x+1, y, z+1$ ; k:  $x-1, y, z-1$ .

*As* sites with variable occupancy in the refinement: *As*(2) and *As*(3), which were partly occupied [1.6(3) and 1.0(3) e, respectively]. Two diffuse maxima within the interlayer were identified as disordered (H<sub>2</sub>O) groups, and assignment of the O scattering factor to the O(7) and O(8) sites gave refined occupancies of 0.96(8) and

0.91(9), respectively. We consider the O(7) site to be fully occupied by an (H<sub>2</sub>O) group. The O(8) site is located near (<2 Å) the *As*(2) and *As*(3) sites, and mutual occupancy of either *As*(2) or *As*(3) by  $As^{3+}$  and the O(8) site by (H<sub>2</sub>O) is unlikely. The combined occupancy of  $As^{3+}$  at *As*(2) and *As*(3) is 0.079(16), and the refined O(8)

TABLE 6. Bond-valence table (vu) for ianbruceite.

	<i>As</i> (1)	<i>Zn</i> (1)	<i>Zn</i> (2)	Σ	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	Σ
O(1)	1.25	0.39	0.45	2.09								2.09
O(2)		0.34		0.34		0.8	0.8					1.94
O(3)	1.32			1.32		0.2	0.2	0.2				1.92
O(4)		0.29	0.51	1.34	0.8							2.14
			0.54									
O(5)	1.15	0.26	0.19	1.86								1.86
		0.26										
O(6)	1.25	0.36	0.33	1.94								1.94
O(7)								0.8	0.8	0.2	0.2	2.00
O(8)					0.2				0.2	0.8	0.8	2.00
Σ	4.97	1.90	2.02		1.0	1.0	1.0	1.0	1.0	1.0	1.0	

Bond-valence parameters in valence units (vu) from Brown and Altermatt (1985).

site occupancy is 0.91(9), this is in accord with a formula containing  $\text{As}_x^{3+}$  and  $(\text{H}_2\text{O})_{1-x}$ , in which  $x \sim 0.08$ . The structure refinement converged to a final  $R_1$  index of 8.6%. The high  $R_1$  value is due to the extreme stacking disorder along the **a** axis. Refined atom coordinates and anisotropic-displacement parameters are listed in Table 4, selected interatomic distances are given in Table 5, and bond valences, calculated using the parameters of Brown and Altermatt (1985), are given in Table 6.

A second dataset was collected on a Nonius kappa CCD 4-circle diffractometer with MoK $\alpha$  radiation; experimental details are given in Table 3. A structural model was obtained using *Sir92* in space group  $P2_1/c$ . The structure refinement converged to a residual of 12.4% for the observed reflections, with isotropic-displacement parameters for all oxygen atoms. The refined atom coordinates and interatomic distances are similar to those listed in Tables 4 and 5.

## Crystal structure

### Coordination of cations

In the structure of ianbruceite, *As*(1) is tetrahedrally coordinated with  $\langle \text{As}-\text{O} \rangle = 1.687 \text{ \AA}$ , which is typical of  $\text{As}^{5+}$  in tetrahedral coordination [e.g. adamite: 1.681  $\text{ \AA}$  (Hawthorne, 1976*a*); scorodite: 1.680  $\text{ \AA}$  (Hawthorne, 1976*b*)]. Zinc is present in two coordinations (Fig. 3), [6]-coordinated [octahedral: *Zn*(1)] and [5]-coordinated [triangular bipyramidal: *Zn*(2)], with  $\langle [6]\text{Zn}-\text{O} \rangle$

$= 2.135$  and  $\langle [5]\text{Zn}-\text{O} \rangle = 2.064 \text{ \AA}$ , respectively. The *Zn*(1) site is coordinated by  $\text{O}_4(\text{OH})(\text{H}_2\text{O})$  and the *Zn*(2) site by  $\text{O}_3(\text{OH})_2$ .

### Structure topology

The  $(\text{Zn}\varphi_5)$  ( $\varphi = \text{O}, \text{OH}, \text{H}_2\text{O}$ ) polyhedra share (OH) vertices to form  $[\text{Zn}\varphi_4]$  chains that extend in the **c** direction (Fig. 4, green). These  $[\text{Zn}\varphi_4]$  chains are decorated by  $(\text{Zn}\varphi_6)$  octahedra (Fig. 4, blue), each of which shares edges with adjacent  $(\text{Zn}\varphi_5)$  triangular bipyramids to form zigzag  $[\text{Zn}^{[5]}\text{Zn}^{[6]}\text{Zn}\varphi_7]$  chains that extend in the **c** direction. These zigzag chains are linked in the **b** direction by sharing corners with  $(\text{AsO}_4)$  tetrahedra (Fig. 4, orange) to form sheets one polyhedron thick in the **a** direction. Note that the presence of tetrahedra and triangular bipyramids imparts a polarity to this single-layer sheet. Two of these sheets with opposite polarity link in the **a** direction by sharing edges between  $(\text{Zn}\varphi_6)$  octahedra and vertices between both Zn polyhedra and As tetrahedra to form a structural unit of composition  $[\text{Zn}_2(\text{OH})(\text{H}_2\text{O})(\text{AsO}_4)]$ . This slab is shown face-on in Fig. 4 and edge-on in Fig. 5.

These  $[\text{Zn}_2(\text{OH})(\text{H}_2\text{O})(\text{AsO}_4)]$  slabs stack along the **a** direction as shown in Fig. 5. The separation of adjacent slabs is  $\sim 4.7 \text{ \AA}$  and two positionally disordered  $(\text{H}_2\text{O})$  groups [O(7) and O(8)] occupy the interstitial space. The  $(\text{H}_2\text{O})$  group associated with the  $(\text{Zn}\varphi_6)$  octahedron, the O(3) vertex of the  $(\text{AsO}_4)$  tetrahedron, and the (OH) group, are all situated at the margins of the

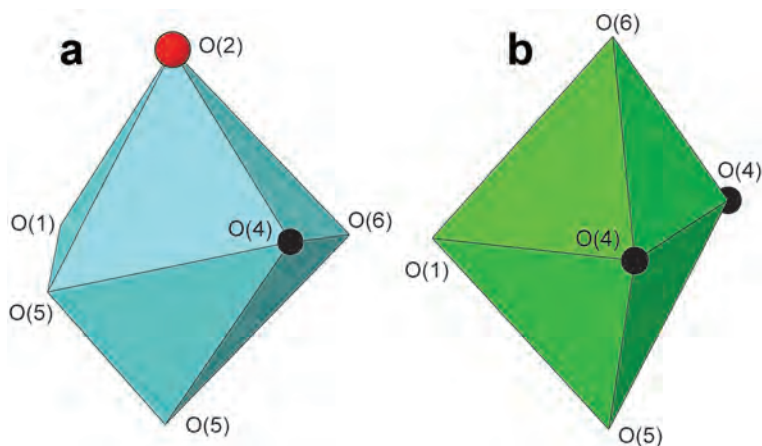


FIG. 3. The Zn polyhedra in ianbruceite; (a) the  $(\text{Zn}(1)\text{O}_4(\text{OH})(\text{H}_2\text{O}))$  octahedron (blue); (b) the  $(\text{Zn}(2)\text{O}_3(\text{OH})_2)$  triangular bipyramid (green). The (OH) groups are shown as black circles and the  $(\text{H}_2\text{O})$  groups as red circles.



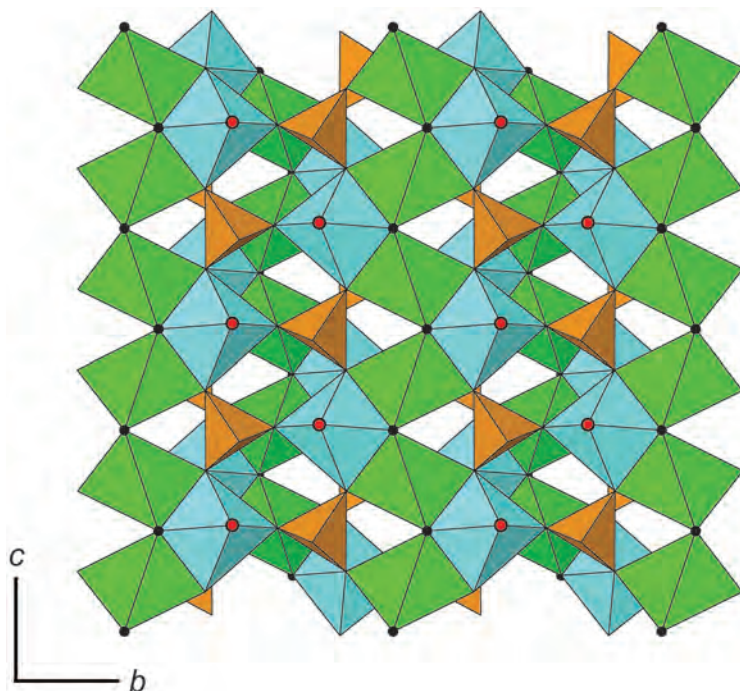


FIG. 4. The crystal structure of ianbruceite projected onto (100), showing the connectivity of the  $[\text{Zn}_2(\text{OH})(\text{H}_2\text{O})(\text{AsO}_4)]$  slab. The  $(\text{Zn}(1)\text{O}_4(\text{OH})(\text{H}_2\text{O}))$  octahedra are blue;  $(\text{Zn}(2)\text{O}_3(\text{OH})_2)$  trigonal bipyramids are green;  $(\text{AsO}_4)$  groups are orange;  $(\text{OH})$  groups are black circles; and  $(\text{H}_2\text{O})$  groups are red circles.

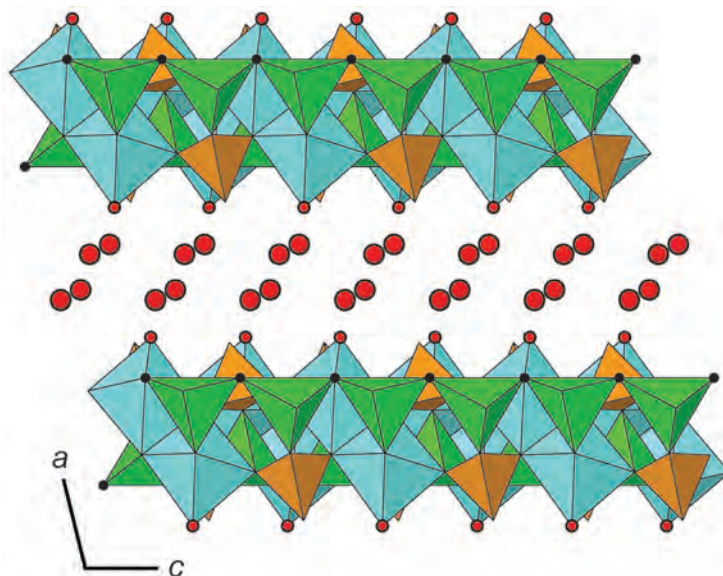


FIG. 5. The crystal structure of ianbruceite projected onto (010), showing the stacking of the  $[\text{Zn}_2(\text{OH})(\text{H}_2\text{O})(\text{AsO}_4)]$  slabs in the  $a$  direction. The  $(\text{Zn}(1)\text{O}_4(\text{OH})(\text{H}_2\text{O}))$  octahedra are blue;  $(\text{Zn}(2)\text{O}_3(\text{OH})_2)$  trigonal bipyramids are green;  $(\text{AsO}_4)$  groups are orange;  $(\text{OH})$  groups are black circles; bonded  $(\text{H}_2\text{O})$  groups are small red circles; and interstitial  $(\text{H}_2\text{O})$  groups are large red circles.

[Zn<sub>2</sub>(OH)(H<sub>2</sub>O)(AsO<sub>4</sub>)] slab and are involved in mutual hydrogen bonding with the interstitial (H<sub>2</sub>O) groups. The weakness of the inter-slab bonding accounts for the extreme disorder in the stacking of the slabs (and the strong streaking along *a*\* observed in the diffraction pattern), and is consistent with the perfect {100} cleavage and the flexible but non-elastic behaviour of thin flakes of the mineral.

#### Anion identities and hydrogen bonding

There are eight crystallographically distinct anions, O(1)–O(8) (Table 4). Inspection of the bond-valence table (Table 6) shows that the bond valence incident at O(2) is 0.34 vu and hence O(2) is an (H<sub>2</sub>O) group. The bond valence incident at O(3) from As<sup>5+</sup> alone is 1.32 vu and the O(3) anion receives bond valence from three additional hydrogen bonds: two from neighbouring (H<sub>2</sub>O) groups at O(2) along the surface of the [Zn<sub>2</sub>(OH)(H<sub>2</sub>O)(AsO<sub>4</sub>)] slab (Fig. 6) and one from the interstitial (H<sub>2</sub>O) group at O(7) (Fig. 7). The O(4) anion bonds to three Zn atoms and is an (OH) group; it directs a hydrogen bond toward the interstitial (H<sub>2</sub>O) group at O(8). Additional mutual hydrogen bonding occurs between the two interstitial (H<sub>2</sub>O) groups at O(7) and O(8) (Table 6; Fig. 7).

We identified two partly occupied As sites, As(2) and As(3) that are close together (Table 5) and cannot be occupied simultaneously. Thus either of them will contribute bond valence to the adjacent O(4) anion. The sum of the bond valence incident at O(4) from the cations of the structural unit is 1.34 vu (Table 6), indicating that a further bond valence of ~0.66 vu is needed to satisfy the valence-sum rule. This value is too low for [<sup>41</sup>As<sup>5+</sup> but is typical for the short bonds of lone-pair stereoactive As<sup>3+</sup>, and hence we assign As<sup>3+</sup> to the As(2) and As(3) sites. Where As<sup>3+</sup> is locally bonded to O(4), the latter is O<sup>2-</sup> in accord with the local version of the valence-sum rule (Hawthorne, 1997). Electroneutrality requires additional anions to neutralize the charge and coordinate the interstitial As<sup>3+</sup>, these are two additional (OH) groups forming an [As<sup>3+</sup>(OH)<sub>2</sub>O] triangular pyramid with As<sup>3+</sup> showing stereoactive lone-pair behaviour. The adjacent interstitial (H<sub>2</sub>O) group at O(8) is situated <2 Å from As(2) and As(3), and this (H<sub>2</sub>O) group is locally absent if the [As<sup>3+</sup>(OH)<sub>2</sub>O] group is present. Thus, if As<sup>3+</sup> is absent, O(4) = (OH) and O(8) = (H<sub>2</sub>O); if As<sup>3+</sup> is present, it is part of an

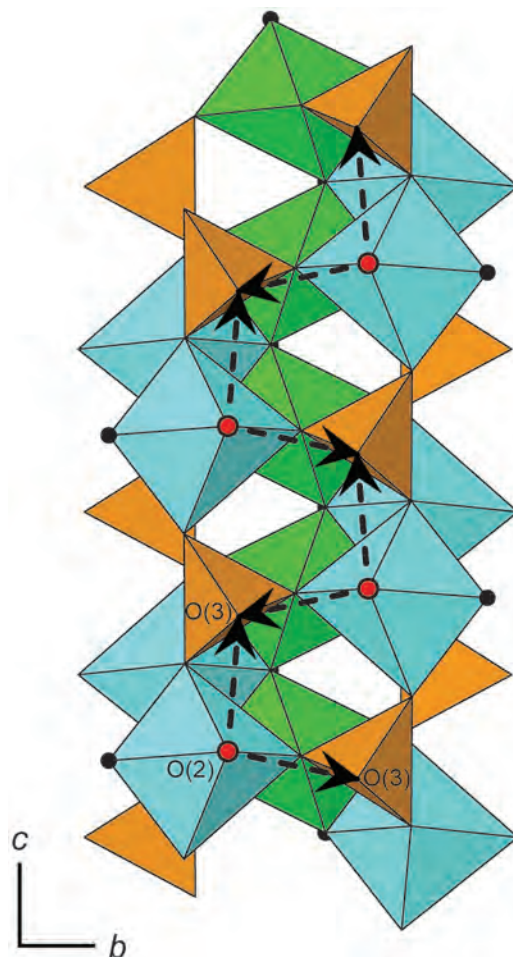


FIG. 6. The crystal structure of ianbruceite projected onto (100), showing hydrogen bonding along the surface of the [Zn<sub>2</sub>(OH)(H<sub>2</sub>O)(AsO<sub>4</sub>)] slab. The (Zn(1)O<sub>4</sub>(OH)(H<sub>2</sub>O)) octahedra are blue; (Zn(2)O<sub>3</sub>(OH)<sub>2</sub>) trigonal bipyramids are green; (AsO<sub>4</sub>) groups are orange; (OH) groups are black circles and (H<sub>2</sub>O) groups are red circles; and hydrogen bonds are shown as dashed lines with arrows to the acceptor anions.

[As<sup>3+</sup>(OH)<sub>2</sub>O] group in which O(4) = O, two additional (OH) groups are present, and O(8) = □. The net substitution is [As<sup>3+</sup>(OH)<sub>2</sub>O<sup>(4)</sup>O]<sup>-</sup> + O<sup>(8)</sup>□ ↔ O<sup>(4)</sup>(OH)<sup>-</sup> + O<sup>(8)</sup>(H<sub>2</sub>O). We calculated [As<sup>3+</sup>(OH)<sub>2</sub>O]<sub>0.04</sub> for the crystal analysed by electron-microprobe and [As<sup>3+</sup>(OH)<sub>2</sub>O]<sub>0.08</sub> for the crystal analysed by structure refinement.

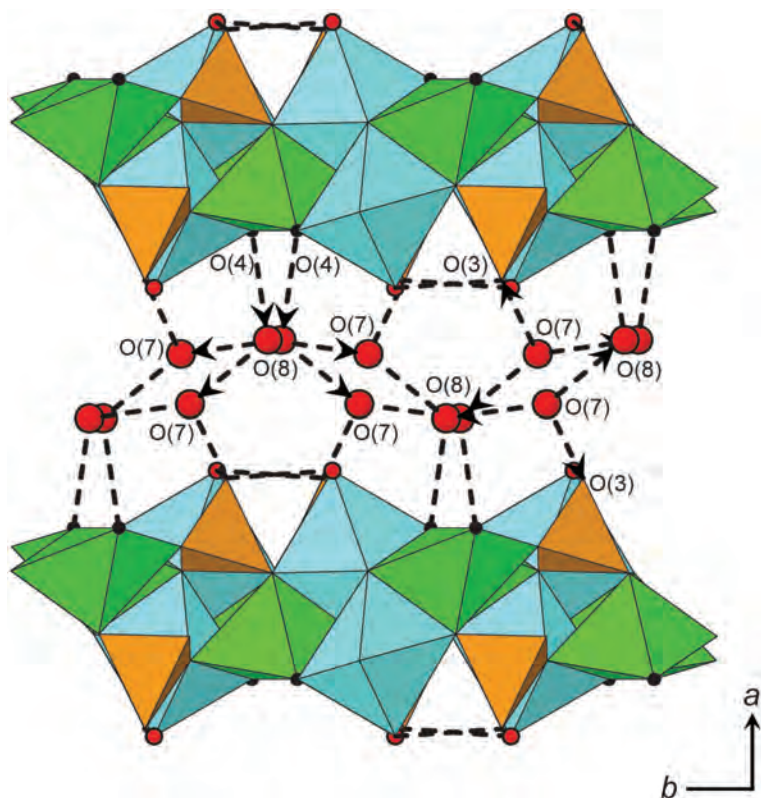


FIG. 7. The crystal structure of ianbruceite projected down [001], showing the hydrogen bonding between the  $[\text{Zn}_2(\text{OH})(\text{H}_2\text{O})(\text{AsO}_4)]$  slabs. The  $(\text{Zn}(1)\text{O}_4(\text{OH})(\text{H}_2\text{O}))$  octahedra are blue;  $(\text{Zn}(2)\text{O}_3(\text{OH})_2)$  trigonal bipyramids are green;  $(\text{AsO}_4)$  groups are orange;  $(\text{OH})$  groups are black circles;  $(\text{H}_2\text{O})$  groups are small red circles; interstitial  $(\text{H}_2\text{O})$  groups are large red circles; and hydrogen bonds are shown as dashed lines with arrows to the acceptor anions.

### Related minerals

Ianbruceite is not isostructural with any other mineral. There are six other hydrated Zn-arsenate minerals: koritnigite (Keller *et al.*, 1980); köttigite (Hill, 1979); arsenohopeite (Neuhold, *et al.*, 2012); davidlloydite (Hawthorne *et al.*, 2012); warikahnite (Riffel *et al.*, 1980); and legrandite (McLean *et al.*, 1971; Pushcharovskii *et al.*, 1971), all of which occur at Tsumeb. Selected properties of these minerals are listed in Table 7. Koritnigite and köttigite have layer structures but the layers are held together by hydrogen bonding with no interstitial  $(\text{H}_2\text{O})$  groups. The only difference between the formulae of legrandite and ianbruceite is the two additional  $(\text{H}_2\text{O})$  groups in ianbruceite. If the chemical formula of euchroite,  $\text{Cu}_2^+(\text{AsO}_4)(\text{OH})(\text{H}_2\text{O})_3$ , is compared with the formula of ianbruceite, it is easy to see how ianbruceite could be mistakenly described as

a Zn analogue of euchroite. Both legrandite and euchroite lack interstitial  $(\text{H}_2\text{O})$  groups and have framework structures that are very different from the layer structure of ianbruceite. The different roles of  $(\text{H}_2\text{O})$  in mineral structures are easily indicated in formulae by separating the different kinds of  $(\text{H}_2\text{O})$  groups, [i.e. those that bond to the structural unit, and those that are interstitial (Hawthorne 1985, 1990, 1992)]. It is logical to place  $(\text{H}_2\text{O})$  belonging to the structural unit in that part of the formula, following the cation(s) that bond(s) to these  $(\text{H}_2\text{O})$  groups (i.e. after Zn for the minerals listed in Table 7); interstitial  $(\text{H}_2\text{O})$  is placed outside the square brackets indicating the structural unit, at the end of the formula. In this way, the structural distinction between ianbruceite and the other hydrated Zn-arsenates in Table 7 (and euchroite) is conveyed by their chemical formulae.

TABLE 7. Comparative data for hydrated zinc arsenates.

	Ianbruceite	Koritnigite	Köttigite	Arsenohopelite	Davidlloydite	Warikahnite	Legrandite
Formula	$[\text{Zn}_2(\text{OH})(\text{H}_2\text{O})(\text{AsO}_4)](\text{H}_2\text{O})_2$	$\text{Zn}(\text{H}_2\text{O})(\text{AsO}_3\text{OH})$	$\text{Zn}_3(\text{H}_2\text{O})_8(\text{AsO}_4)_2$	$\text{Zn}_3(\text{H}_2\text{O})_4(\text{AsO}_4)_2$	$\text{Zn}_3(\text{H}_2\text{O})_4(\text{AsO}_4)_2$	$\text{Zn}_3(\text{H}_2\text{O})_2(\text{AsO}_4)_2$	$\text{Zn}_2(\text{OH})(\text{H}_2\text{O})(\text{AsO}_4)$
Zn:As ratio	2:1	1:1	3:2	3:2	3:2	3:2	2:1
Symmetry	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/m$	$Pmma$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
$a$ (Å)	11.793	7.948	10.241	10.804	5.976	6.710	12.805
$b$	9.114	15.829	13.405	19.003	7.600	8.989	7.933
$c$	6.827	6.668	4.757	5.112	5.447	14.533	10.215
$\alpha$ (°)	90	90.86	90	90	84.29	105.59	90
$\beta$	103.86	96.56	105.21	90	90.49	93.44	104.39
$\gamma$	90	90.05	90	90	88.00	108.68	90
$V$ (Å <sup>3</sup> )	712.3	833.3	630.2	1049.5	246.0	789.5	1005.1
$Z$	4	8	2	4	1	4	8
$D$ (g cm <sup>-3</sup> )	3.20	3.56	3.26	3.46	3.66	4.29	4.03
Structure type	Layer	Layer	Layer	Layer	Layer	Framework	Framework
Interlayer type	(open; free H <sub>2</sub> O)	(open)	(open)	(octahedral bridge)	(octahedral bridge)	—	—
Interlayer gap* (Å)	4.70	1.82	0.64	—	—	—	—

\* The minimum orthogonal distance across the interlayer, measured from oxygen centres.



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Refinement of  $F^2$  against ALL reflections. The weighted R-factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional R-factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is

not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and R-factors based on ALL data will be even larger.

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All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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As O2 3.609(12) 3_666 ?
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As2 O2 As3 5.6(10) 1\_545 1\_545 ?  
O4 O2 As3 27.0(8) 1\_545 1\_545 ?  
O1 O2 As3 117.1(9) 2\_645 1\_545 ?  
O7 O2 As3 77.3(10) 3\_665 1\_545 ?  
O6 O2 As3 69.0(8) 3\_655 1\_545 ?  
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As O3 O2 103.2(6) . 3\_666 ?  
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As3 O4 Zn2 90.8(15) . 4\_576 ?  
As2 O4 Zn2 109.1(10) . . ?  
As3 O4 Zn2 97.2(15) . . ?  
Zn2 O4 Zn2 123.1(6) 4\_576 . ?  
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As3 O4 Zn1 148.7(18) . 1\_565 ?  
Zn2 O4 Zn1 104.4(5) 4\_576 1\_565 ?  
Zn2 O4 Zn1 97.0(4) . 1\_565 ?

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As3 O4 O6 124.2(15) . 3\_665 ?  
Zn2 O4 O6 144.2(7) 4\_576 3\_665 ?  
Zn2 O4 O6 52.2(3) . 3\_665 ?  
Zn1 O4 O6 50.0(3) 1\_565 3\_665 ?  
As2 O4 O5 119.0(11) . 3\_666 ?  
As3 O4 O5 130.5(15) . 3\_666 ?  
Zn2 O4 O5 54.8(3) 4\_576 3\_666 ?  
Zn2 O4 O5 130.4(6) . 3\_666 ?  
Zn1 O4 O5 50.6(3) 1\_565 3\_666 ?  
O6 O4 O5 99.0(5) 3\_665 3\_666 ?  
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As3 O4 O8 35.0(19) . . ?  
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Zn2 O4 O8 116.2(12) . . ?  
Zn1 O4 O8 113.9(9) 1\_565 . ?  
O6 O4 O8 111.1(11) 3\_665 . ?  
O5 O4 O8 111.8(12) 3\_666 . ?  
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As3 O4 O2 102.6(18) . 1\_565 ?  
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O5 O4 O2 69.9(4) 3\_666 1\_565 ?  
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Zn2 O4 As3 44.9(8) . 4\_575 ?  
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O6 O4 As3 47.8(8) 3\_665 4\_575 ?  
O5 O4 As3 144.4(9) 3\_666 4\_575 ?  
O8 O4 As3 77.1(14) . 4\_575 ?  
O2 O4 As3 83.4(9) 1\_565 4\_575 ?  
O6 O4 As3 117.6(9) 2\_655 4\_575 ?  
As2 O4 O4 87.3(9) . 4\_575 ?  
As3 O4 O4 79.1(15) . 4\_575 ?  
Zn2 O4 O4 135.0(6) 4\_576 4\_575 ?  
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O6 O4 O4 97.4(5) 2\_655 4\_575 ?  
As3 O4 O4 27.5(8) 4\_575 4\_575 ?  
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As O5 O4 130.8(7) 1\_545 3\_666 ?  
Zn1 O5 O4 49.1(3) 3\_656 3\_666 ?  
Zn1 O5 O4 106.7(5) . 3\_666 ?  
Zn2 O5 O4 42.9(3) 2\_645 3\_666 ?  
As O6 Zn1 135.1(6) 1\_545 3\_655 ?  
As O6 Zn2 130.3(6) 1\_545 3\_665 ?  
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O4 As2 Zn2 39.4(7) . . ?  
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O2 As2 Zn2 93.4(8) 1\_565 . ?  
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As2 As3 O8 44(3) . . ?  
O4 As3 O8 111(3) . . ?  
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O8 As3 Zn2 118(3) . 4\_576 ?  
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Zn2 As3 As 77.3(12) . 2\_645 ?  
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 Zn2 As3 O2 79.8(11) . 1\_565 ?  
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 As2 As3 O4 96(3) . 4\_575 ?  
 O4 As3 O4 73.8(15) . 4\_575 ?  
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 Zn2 As3 O4 109.1(15) 4\_576 4\_575 ?  
 Zn2 As3 O4 30.9(5) . 4\_575 ?  
 As As3 O4 76.7(10) 2\_645 4\_575 ?  
 O4 As3 O4 139.8(15) 4\_576 4\_575 ?  
 O2 As3 O4 93.1(11) 1\_565 4\_575 ?  
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