Structural Chemistry of Copper and Zinc Minerals. VI. Bayldonite, (Cu,Zn)₃Pb(AsO₄)₂(OH)₂: A Complex Layer Structure

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Abstract

Bayldonite, (Cu,Zn)₃Pb(AsO₄)₂(OH)₂ from Tsumeb, S.W. Africa, is monoclinic, space group C2/c, with cell dimensions: a = 10.147(2), b = 5.892(1), c =14.081 (2) Å, $\beta = 106.05$ (1)° and Z = 4. The crystal structure has been determined by the heavy-atom method and refined by the full-matrix least-squares method to an R factor of 0.053 for 1057 observed Xray reflections. The crystal structure of bayldonite consists of interconnected Cu octahedral layers and lead arsenate polyhedral-tetrahedral layers which alternate along the c axis, giving rise to complex pseudohexagonal layers parallel to (001). The Cu octahedral sheet, with six-membered octahedral rings, is formed by three crystallographically independent $[CuO_4(OH)_2]$ octahedra with point symmetry 1, showing Jahn-Teller distortion; the square-planar Cu-O (or OH) distances vary from 1.878 to 2.087 Å (average 1.970 Å), whereas the apical Cu-O distances vary from 2.272 to 2.474 Å. The PbO₈ polyhedron is a square antiprism with an average Pb-O bond length of 2.722 Å. The tetrahedral As-O bond lengths vary from 1.66 to 1.724 Å (average 1.696 Å). The H atom appears to be disordered between the (OH) group and a highly charge-deficient O atom, which is bonded to one Pb atom, in addition to the As atom. The observed twinning, cleavage and crystal habit result from the pseudohexagonal nature of the layer structure.

Introduction

As a part of our investigation on the structural chemistry of copper and zinc minerals, we have determined the crystal structure of bayldonite, $(Cu,Zn)_3$ -Pb(AsO₄)₂(OH)₂ from Tsumeb, S.W. Africa, a mineral with partial substitution of Cu by Zn atoms. Bayldonite was first described by Church (1865) as a basic copper lead arsenate from copper mines near St Day, Cornwall, England. It has been subsequently found in Tsumeb, S.W. Africa, (Biehl, 1919), and several localities in France (Guillemin, 1956). It usually occurs 0567-7408/79/040819-05\$01.00 as apple-green minute mammillary concretions with a micaceous or fibrous structure; also massive finegranular to powdery and as crusts in association with mimetite, olivenite, azurite and malachite. Based on poor-quality single crystals from La Rabasse, Ceilhes, Hérault, France, Guillemin (1956) determined the chemical composition as $Cu_3Pb(AsO_4)_2(OH)_2$ and the crystal system to be monoclinic with approximate cell dimensions. In 1973, well-formed sharp dark-green 'scalenohedral' bayldonite crystals were discovered at Tsumeb from an arsenate-rich zone in tennantite, in association with adamite, cuproadamite, olivenite, schultenite, tsumcorite, kevite and duftite (Pinch & Wilson, 1977). Using these 'scalenohedra', which, in fact, consist of three twinned individuals, Cesbron & Vachey (1974) determined the unit-cell dimensions and the space group; the a and c dimensions turned out to be twice the dimensions reported by Guillemin (1956).

Crystal data

A single-crystal fragment of dark-green bayldonite from Tsumeb (NMNH No. 136811) was ground to a sphere with a diameter of 0.125 mm using the sphere grinder (Bond, 1951). The single-crystal sphere was mounted on the Syntex $P\bar{1}$ automatic single-crystal Xray diffractometer. The unit-cell dimensions were refined by the least-squares method based on 15 reflections with 2θ values between 25 and 35° measured with Mo $K\alpha$ radiation on the diffractometer (Table 1). These cell dimensions are in good agreement

Table 1. Bayldonite: crystal data

Bayldonite $(Cu,Zn)_3Pb(AsO_4)_2(OH)_2^*$ Dark green 'scalenohedra', Tsumeb, S.W. Africa NMNH No. 136811 Monoclinic, 2/m Cell volume: $809 \cdot 05$ (23) Å³ $a = 10 \cdot 147$ (2) Å Cell content: $4[(Cu,Zn)_3Pb(AsO_4)_2(OH)_2]$ $b = 5 \cdot 892$ (1) $D_m = 5 \cdot 65$ Mg m⁻³ $c = 14 \cdot 081$ (2) $D_c = 5 \cdot 707$ $\beta = 106 \cdot 05$ (1)° μ (Mo $K\alpha$) = 37 \cdot 161 mm⁻¹ Space group C2/c

* Contains 1.1 wt % ZnO (Cesbron & Vachey, 1974). © 1979 International Union of Crystallography with those determined by Cesbron & Vachey (1974). Of the two possible space groups C2/c and Cc, the centrosymmetric space group C2/c has been confirmed by the crystal-structure determination.

Collection of intensity data

The X-ray intensity data were collected from the singlecrystal sphere by the θ -2 θ scan method on the automatic single-crystal diffractometer (Syntex *P*1). Mo K α radiation, monochromatized by reflection from a graphite 'single' crystal and a scintillation counter were used for the intensity measurement by the variable scan method, the minimum scan rate being 1° min⁻¹ (50 kV, 17.5 mA). All reflections within $2\theta \le 65^\circ$ were measured – a total of 1526 reflections, out of which 464 were below $3\sigma(I)$, where $\sigma(I)$ is the standard deviation of the measurement of the intensity, *I*, as determined by the counting statistics. The intensity data were corrected for Lorentz, polarization and absorption factors.

Determination and refinement of the structure

The positions of the Pb, Cu and As atoms were determined from a three-dimensional Patterson synthesis. A difference Fourier synthesis, based on the heavy-atom positions, indicated the positions of the O atoms. The refinement of the structure was carried out by the fullmatrix least-squares method using the program RFINE (Finger, 1969) based on reflections with $F_o > 3\sigma(F_o)$. The scattering factors for Pb, Cu, As, O and H were taken from Cromer & Mann (1968), which were corrected for anomalous dispersion (Cromer & Liberman, 1970). The observed structure factors (F_{o} 's) were weighted by $1/\sigma^2(F_o)$, where $\sigma(F_o)$ is the standard deviation of the measurement of F_{o} . Four cycles of refinement using isotropic temperature factors, followed by three more cycles with anisotropic temperature factors using only the observed reflections resulted in an R factor of 0.055. Five very strong reflections presumed to be affected by extinction or measurement errors were eliminated from the refinement at this stage. Two further cycles of refinement using anisotropic temperature factors yielded an R of 0.053 for 1057 observed reflections. A difference Fourier synthesis revealed two possible H atom positions, only one of which refined satisfactorily. The final R factor remained unchanged. The positional and isotropic thermal parameters are listed in Table 2.* Bond lengths and angles with their standard deviations, which include the

Table 2. Bayldonite, (Cu,Zn)₃Pb(AsO₄)₂(OH)₂: atomic positional and thermal parameters, with standard deviations in parentheses

	x	r	Ζ	$B_{eq} (A^2)^*$
Cu(1)	0.0000	0.0000	0.0000	0.66 (3)
Cu(2)	0.5000	0.0000	0.0000	0.55 (3)
Cu(3)	0.2500	0.2500	0.5000	0.58 (3)
Pb	0.0000	0.2698 (2)	0.2500	1.19 (2)
As	0.2974 (1)	0.2164 (2)	0.1405 (1)	0.40 (2)
D(1)	0.3672 (8)	0.4590 (14)	0.1179 (7)	0.70(12)
D(2)	0.1419 (8)	0.4986 (14)	0.4174 (7)	0.69 (12)
D(3)	0.1215 (8)	0.2212(15)	0.0971 (6)	0.96 (12)
D(4)	0.3413(11)	0.1260 (15)	0.2578 (6)	1.40 (16)
OH)	0.3960 (8)	0.2487(12)	0.4373(5)	0.39(9)
H	0.380 (16)	0.109 (31)	0.354 (13)	2.5 (4.1)

* Equivalent isotropic temperature factor, calculated from anisotropic temperature factor coefficients (Hamilton, 1959).

standard errors of the measurement of unit-cell dimensions, are listed in Table 3. The average standard deviations of Pb–O, Cu–O and As–O bond lengths are 0.008 Å, and those in O–Pb–O, O–Cu–O and O–As–O angles, 0.2, 0.3 and 0.4° respectively.

Description of the structure

The crystal structure of bayldonite consists of two different interconnected sheets with pronounced pseudohexagonal symmetry: (a) a copper octahedral sheet, and (b) a lead arsenate sheet, both parallel to the (001) plane (Fig. 1).

(a) The copper octahedral sheet

Cu(1) and Cu(2) octahedra form a chain parallel to the *b* axis by sharing opposite octahedral edges [O(3)-



Fig. 1. Stereoscopic view of the bayldonite $(Cu,Zn)_3Pb(AsO_4)_2^-$ (OH)₂ structure. Note the alternating Cu octahedral sheet and the Pb-arsenate sheet along the *c* axis.

^{*} Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34148 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bayldonite, (Cu,Zn)₃Pb(AsO₄)₂(OH)₂: interatomic distances (Å) and angles (°), with standard deviations in parentheses

The Cu(1) octa	hedron						
Cu(1)-O(1) Cu(1)-O(3) Cu(1)-(OH) Mean	2.423 (10) (×2) 2.039 (8) (×2) 1.891 (7) (×2) 2.118	O(1)-Cu(1)-O(3) O(1)-Cu(1)-(OH) O(1)-Cu(1)-O(3') O(1)-Cu(1)-(OH)' O(3)-Cu(1)-(OH)'	87.2 (3) (×2) 93.1 (3) (×2) 92.8 (3) (×2) 86.9 (3) (×2) 88.2 (3) (×2)				
O(1)-O(3) O(1)-(OH) O(1)-O(3') O(1)-(OH)' O(3)-(OH) O(3)-(OH)'	3.09 (1) (×2) 3.15 (1) (×2) 3.24 (1) (×2) 3.08 (1) (×2) 2.74 (1) (×2) 2.83 (1) (×2)	O(3)-Cu(1)-(OH)' Mean	91.9 (3) (×2) 90.0				
The Cu(2) octahedron							
Cu(2)-O(3) Cu(2)-O(2) Cu(2)-(OH) Mean	2·272 (9) (×2) 2·087 (10) (×2) 1·878 (7) (×2) 2·079	O(3)-Cu(2)-O(2) O(3)-Cu(2)-(OH) O(3)-Cu(2)-O(2)' O(3)-Cu(2)-(OH)' O(2)-Cu(2)-(OH)'	90.3 (3) (×2) 81.9 (3) (×2) 89.7 (3) (×2) 98.1 (3) (×2) 82.8 (3) (×2)				
O(3)-O(2) O(3)-(OH) O(3)-O(2') O(3)-(OH)' O(2)-(OH) O(2)-(OH)'	3.09 (1) (×2) 2.74 (1) (×2) 3.08 (1) (×2) 3.15 (1) (×2) 2.63 (1) (×2) 2.98 (1) (×2)	O(2)-Cu(2)-(OH)' Mean	97·2 (3) (×2) 90·0				
The Cu(3) octa	hedron						
Cu(3)-O(1) Cu(3)-O(2) Cu(3)-(OH) Mean	2·454 (8) (×2) 2·000 (8) (×2) 1·924 (9) (×2) 2·126	O(1)-Cu(3)-O(2) O(1)-Cu(3)-(OH) O(1)-Cu(3)-O(2)' O(1)-Cu(3)-(OH)' O(2)-Cu(3)-(OH)	88.1 (3) (×2) 88.7 (3) (×2) 91.9 (3) (×2) 91.3 (3) (×2) 96.0 (3) (×2)				
O(1)-O(2) O(1)-(OH) O(1)-O(2') O(1)-(OH)' O(2)-(OH) O(2)-(OH)'	$\begin{array}{c} 3 \cdot 11 \ (1) \ (\times 2) \\ 3 \cdot 08 \ (1) \ (\times 2) \\ 3 \cdot 22 \ (1) \ (\times 2) \\ 3 \cdot 15 \ (1) \ (\times 2) \\ 2 \cdot 98 \ (1) \ (\times 2) \\ 2 \cdot 92 \ (1) \ (\times 2) \end{array}$	O(2)–Cu(3)–(OH)' Mean	84·0 (3) (×2) 90·0				
The Pb polyhed	dron						
Pb-O(1) Pb-O(2) Pb-O(3) Pb-O(4) Mean	2.693 (8) (×2) 2.752 (9) (×2) 2.776 (9) (×2) 2.668 (10) (×2) 2.722	O(1)-Pb-O(2) O(1)-Pb-O(3) O(1)-Pb-O(4) O(2)-Pb-O(3) O(2)-Pb-O(4) O(2)-Pb-O(4)	72.4 (3) (x2) 102.8 (3) (x2) 111.8 (3) (x2) 118.4 (2) (x2) 58.0 (2) (x2) 60.2 (2) (x2)				
$\begin{array}{c} O(1)-O(2)\\ O(1)-O(3)\\ O(1)-(4)\\ O(2)-O(3)\\ O(2)-O(4)\\ O(3)-O(4)\\ O(1')-O(2)\\ O(1')-O(3)\\ O(1')-O(3)\\ O(1')-O(4)\\ O(2')-O(3)\\ O(2')-O(4)\\ O(2')-O(4)\\ O(4)-O(4')\\ O(2)-O(2')\\ O(3)-O(3')\\ O(4)-O(4') \end{array}$	$\begin{array}{c} 3\cdot22 (1) (\times 2) \\ 4\cdot27 (1) (\times 2) \\ 4\cdot44 (1) (\times 2) \\ 4\cdot45 (1) (\times 2) \\ 2\cdot63 (1) (\times 2) \\ 3\cdot10 (1) (\times 2) \\ 3\cdot09 (1) (\times 2) \\ 3\cdot09 (1) (\times 2) \\ 4\cdot14 (1) (\times 2) \\ 3\cdot08 (1) (\times 2) \\ 3\cdot34 (1) (\times 2) \\ 3\cdot34 (1) (\times 2) \\ 3\cdot34 (1) (\times 2) \\ 3\cdot95 (1) (\times 2) \\ 4\cdot74 (1) (\times 2) \\ 3\cdot95 (1) (\times 2) \\ 4\cdot74 (1) (\times 2) \\ 3\cdot95 (1) (\times 2) \\ 5\cdot52 (1) (\times 2) \\ 3\cdot29 (1) (\times 2) \end{array}$	O(3)-Pb-O(4) O(1')-Pb-O(2) O(1')-Pb-O(3) O(2')-Pb-O(4) O(2')-Pb-O(4) O(3')-Pb-O(4) O(1)-Pb-O(1') O(2)-Pb-O(2') O(3)-Pb-O(3') O(4)-Pb-O(4')	69.3 (3) (x2) 165.7 (2) (x2) 68.8 (2) (x2) 134.4 (3) (x2) 68.0 (3) (x2) 121.1 (3) (x2) 94.2 (4) (x2) 121.3 (3) (x2) 168.2 (4) (x2) 76.1 (4) (x2)				

O(OH) and O(3')-O(OH)']. These chains are crosslinked through the Cu(3) octahedra, which share opposite octahedral edges [O(1)-O(OH) and O(1')-O(OH)'] with two Cu(1) octahedra belonging to two adjacent octahedral chains. An octahedral sheet with holes based on a hexagonal array is formed this way, which contains six-membered octahedral rings (Fig. 2).

Table 3 (cont.)

The $[AsO_4]$ tetrahedron							
As-O(1)	1.666 (8)	O(1)-As-O(2)	108-8 (4)				
As - O(2)	1.724 (8)	O(1)-As- $O(3)$	111.9 (4)				
As - O(3)	1.719 (8)	O(1)-As-O(4)	116-8 (5)				
As = O(4)	1.674 (8)	O(2)-As- $O(3)$	108-4 (4)				
Mean	1.696	O(2)-As- $O(4)$	101-4 (4)				
		O(3)-As- $O(4)$	108-8 (5)				
O(1) - O(2)	2.76 (1)	Mean	109.4				
O(1)-O(3)	2.80 (1)						
O(1)-O(4)	2.85 (1)						
O(2)-O(3)	2·79 (1)						
O(2)–O(4)	2.63 (1)						
O(3)-O(4)	2.76 (1)						
Hydrogen bonds							
(OH)H	1.41 (18)	(OH)-H-O(4)	139 (14)				
O(4)H	1.30 (18)	Cu(1)(OH)H	140 (7)				
(OH)O(4)	2.54 (1)	Cu(2)–(OH)–H	82 (7)				
		Cu(3)(OH)H	117 (7)				
Cation-cation distances (<3.5 Å)							
Cu(1)- $Cu(2)$	2.9485 (5)	As-Cu(1)	3.3685 (10)				
Cu(1) - Cu(3)	2.9341 (5)	As-Cu(2)	3-4681 (10)				
Cu(2) - Cu(3)	2.9341 (5)	As-Cu(3)	3.3446 (10)				
		Pb-As	3-4332 (11)				

Alternatively, the octahedral sheet can be considered as a distorted version of the hydrargillite, $Al(OH)_3$ type sheet. A comparable open octahedral sheet structure has been found in veszelyite, $(Cu,Zn)_2Zn(PO_4).2H_2O$ (Ghose, Leo & Wan, 1974), which contains eightmembered octahedral rings.

(b) The lead arsenate sheet

Pb is coordinated by eight O atoms, the PbO₈ polyhedron being a square antiprism (Fig. 3). Alternating PbO₈ polyhedra and arsenate tetrahedra form a chain parallel to [110] by sharing a corner [O(3)] and an edge [O(2)-O(4)]. These chains are cross-linked to adjacent chains, by sharing a corner [O(1)] between an arsenate tetrahedron and a Pb polyhedron. The result is an open



Fig. 2. The copper octahedral sheet in bayldonite viewed nearly down the c axis. The filled bonds indicate short (~2 Å) bonds. Note the six-membered (pseudohexagonal) ring formed by Cu octahedra, indicated by broken lines.

polyhedral sheet, containing six-membered polyhedral rings, consisting of alternating Pb polyhedra and arsenate tetrahedra (Fig. 4). The lead arsenate polyhedral sheet alternates with the Cu octahedral sheet along the c axis, giving rise to a complex layer structure parallel to (001) (Fig. 1).

Copper arsenate chains

The edge-sharing Cu(1) and Cu(2) octahedra form a chain parallel to the *b* axis; the arsenate tetrahedra share two corners with two adjacent Cu(1) and Cu(2) octahedra, such that an edge of the AsO₄ tetrahedron is parallel to the *b* axis. The periodicity of this Cuarsenate chain in bayldonite is $5 \cdot 893$ Å (Fig. 5). Topologically similar Cu-phosphate, Cu-arsenate and Cu-sulfate chains are present in the structures of tsumebite Pb₂Cu[PO₄SO₄OH] (Nicholls, 1966), Astsumebite Pb₂Cu[AsO₄SO₄(OH)], fornacite Pb₂Cu[AsO₄CrO₄(OH)] (Cocco, Fanfani & Zanazzi, 1967), vauquelinite Pb₂Cu[PO₄CrO₄(OH)] (Fanfani &



Fig. 3. The square-antiprismatic coordination polyhedron around Pb in bayldonite.



Fig. 4. The lead arsenate sheet in bayldonite viewed nearly down the c axis. Note the six-membered (pseudohexagonal) ring, formed by alternating Pb polyhedra and As tetrahedra, indicated by broken lines.

Zanazzi, 1968) and linarite $PbCuSO_4(OH)_2$ (Bachmann & Zemann, 1961). All these minerals are characterized by *b* dimensions which range from 5.65 (linarite) to 5.92 Å (As-tsumebite).

Stereochemistry of the cupric ions and copper-zinc substitution

All the three independent Cu^{2+} ions, occurring in special positions with point symmetry \overline{I} , show the usual Jahn-Teller distortion. Each tetragonally distorted $[CuO_4(OH)_2]$ octahedron consists of two O atoms and two OH ions within the square plane, with two further O atoms at the apices. Within the square plane, Cu-(OH) distances (average 1.898 Å) are significantly shorter than the Cu-O distances (average 2.042 Å). The square-planar Cu-O (or OH) distances show little variation, with an average of 1.970 Å. In contrast, the apical Cu-O distances vary from 2.272 for Cu(2) to 2.423 for Cu(1) and 2.454 Å for Cu(3). Hence, the Cu(3) octahedron is the most and the Cu(2) octahedron the least distorted in terms of bond distances.

The chemical analysis of the bayldonite sample from Tsumeb indicates 1.1 wt% ZnO (Cesbron & Vachey, 1974). Since the octahedral coordination for Zn²⁺ (a d^{10} ion) is expected to be regular, Cu(2) is the most likely site for Zn substitution. In fact, the Cu(2) coordination in bayldonite is closely comparable to the octahedral [ZnO₄(OH)₂] coordination in adamite, Zn₂AsO₄(OH), where the Zn–O distances are 2.051 (×2), 2.062 (×2) and 2.261 Å (×2) (average 2.125 Å) (Hill, 1976; Hawthorne, 1976). Crystal-chemically it seems possible that bayldonite, richer in Zn, may attain a composition of PbCu₂Zn(AsO₄)₂(OH)₂.



Fig. 5. The copper arsenate chain in bayldonite parallel to the *b* axis. The repeat unit of this chain accounts for the b (= 5.892 Å) dimension.

The tetrahedral $[AsO_4]$ ion

The tetrahedral [AsO₄] group, with an average As-O distance of 1.696 Å shows considerable variation in As-O bond lengths (from 1.666 to 1.724 Å) and O-As-O angles (from 101.4 to 116.8°). One of the two short As-O bonds involves O(4), which is further bonded to a Pb atom and is the recipient of a hydrogen bond; the other three O atoms bonded to As are further bonded to one Pb and two Cu atoms each. Within the latter three O atoms, O(1) is involved in two long Cu-O bonds, in addition to a Pb-O bond. In contrast, O(2) is involved in two short Cu-O bonds and a Pb-O bond, whereas O(3) is involved in one short and one long Cu-O bond and a Pb-O bond. Hence, the As-O(1) bond (1.666 Å) is significantly shorter than the As–O(2) (1.723 Å) and As–O(3) (1.719 Å) bonds. In effect, the variation of the As-O bond lengths reflects the variable charges the O atoms are receiving from other cations.

PbO₈ polyhedron

The PbO₈ polyhedron, with point symmetry 2, can be described as a square antiprism (Fig. 3). This coordination is very similar to the eightfold square-antiprismatic coordination for Pb found in nadorite, PbSbO₂Cl (Giuseppetti & Tadini, 1973), PbTiO₃ (Shirane, Pepinsky & Frazer, 1956), and diaboleite Pb₂Cu(OH)₄Cl₂ (Rouse, 1971). In bayldonite, all Pb-O bonds are ionic, since all the Pb-O distances (average 2.722 Å) are larger than the sum of the ionic radii of Pb²⁺ and O²⁻ (2.69 Å) (Shannon & Prewitt, 1969).

Hydrogen bonding

The H atom is expected to be localized near the O atom of the OH group, which is bonded to three Cu atoms. The recipient of the hydrogen bond is the O(4) atom, which is highly charge deficient (1.5 e.v.u. from one As and one Pb) and tends to attract the H atom away from the OH group. The H atom appears to be intermediate in position (most likely disordered) between O(4) and the OH group, the (OH)-H and O(4)-H distances being 1.4 and 1.3 Å respectively.

Twinning, cleavage and habit

Cesbron & Vachey (1974) noted that the dark-green 'scalenohedra' of bayldonite from Tsumeb are in fact trillings, in which two adjacent crystals have [130] in common in the (001) plane. The crystals present sector

twinning in thin sections perpendicular to the pseudothreefold axis, parallel to [001]. Structurally this type of twinning can be explained on the basis of the pseudohexagonal symmetry of both the Cu octahedral sheet and the Pb-arsenate sheet parallel to the (001) plane (Figs. 2 and 4).

Bayldonite possesses a pronounced cleavage parallel to (001), which has not been mentioned previously. This cleavage breaks through four Pb–O bonds, one As–O and one hydrogen bond.

Bayldonite commonly occurs in fine micaceous aggregates composed of platelets parallel to (001). The sheet structure of bayldonite also explains this habit.

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