# Structural Chemistry of Copper and Zinc Minerals. VI. Bayldonite, $(\mathbf{C u}, \mathbf{Z n})_{3} \mathbf{P b}\left(\mathrm{AsO}_{4}\right)_{\mathbf{2}}(\mathbf{O H})_{2}$ : A Complex Layer Structure 

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#### Abstract

Bayldonite, $(\mathrm{Cu}, \mathrm{Zn})_{3} \mathrm{~Pb}\left(\mathrm{AsO}_{4}\right)_{2}(\mathrm{OH})_{2}$ from Tsumeb, S.W. Africa, is monoclinic, space group $C 2 / c$, with cell dimensions: $a=10.147(2), b=5.892(1), c=$ 14.081 (2) $\AA, \beta=106.05$ (1) $)^{\circ}$ 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 $\left[\mathrm{CuO}_{4}(\mathrm{OH})_{2}\right]$ octahedra with point symmetry $\overline{1}$, showing Jahn-Teller distortion; the square-planar $\mathrm{Cu}-\mathrm{O}$ (or OH ) distances vary from 1.878 to $2.087 \AA$ (average $1.970 \AA$ ), whereas the apical $\mathrm{Cu}-\mathrm{O}$ distances vary from 2.272 to $2.474 \AA$. The $\mathrm{PbO}_{8}$ polyhedron is a square antiprism with an average $\mathrm{Pb}-\mathrm{O}$ bond length of $2.722 \AA$. The tetrahedral As-O bond lengths vary from 1.66 to $1.724 \AA$ (average $1.696 \AA$ ). The H atom appears to be disordered between the $(\mathrm{OH})$ 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, $(\mathrm{Cu}, \mathrm{Zn})_{3^{-}}$ $\mathrm{Pb}\left(\mathrm{AsO}_{4}\right)_{2}(\mathrm{OH})_{2}$ 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
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 $\mathrm{Cu}_{3} \mathrm{~Pb}\left(\mathrm{AsO}_{4}\right)_{2}(\mathrm{OH})_{2}$ 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, keyite 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 $P \overline{1}$ automatic single-crystal X ray diffractometer. The unit-cell dimensions were refined by the least-squares method based on 15 reflections with $2 \theta$ values between 25 and $35^{\circ}$ measured with Mo Ka radiation on the diffractometer (Table 1). These cell dimensions are in good agreement

## Table 1. Bayldonite: crystal data

Bayldonite $(\mathrm{Cu}, \mathrm{Zn})_{3} \mathrm{~Pb}\left(\mathrm{AsO}_{4}\right)_{2}(\mathrm{OH})_{2}{ }^{*}$
Dark green 'scalenohedra', Tsumeb, S.W. Africa NMNH No. 136811

Monoclinic, $2 / m \quad$ Cell volume: $809 \cdot 05(23) \AA^{3}$
$a=10 \cdot 147(2) \AA \quad$ Cell content: $4\left[(\mathrm{Cu}, \mathrm{Zn})_{3} \mathrm{~Pb}\left(\mathrm{AsO}_{4}\right)_{2}(\mathrm{OH})_{2}\right]$
$b=5.892(1) \quad D_{m}=5.65 \mathrm{Mg} \mathrm{m}^{-3}$
$c=14.081(2) \quad D_{c}^{m}=5.707$
$\beta=106.05(1)^{\circ} \quad \mu($ Mo $K \alpha)=37.161 \mathrm{~mm}^{-1}$
Space group $C 2 / c$

* Contains $1 \cdot 1$ wt \% ZnO (Cesbron \& Vachey, 1974).
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with those determined by Cesbron \& Vachey (1974). Of the two possible space groups $C 2 / c$ and $C c$, the centrosymmetric space group $C 2 / c$ 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 $\theta-2 \theta$ scan method on the automatic single-crystal diffractometer (Syntex P1). Mo $K a r$ 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 $1^{\circ} \mathrm{min}^{-1}$ ( $50 \mathrm{kV}, 17.5 \mathrm{~mA}$ ). All reflections within $2 \theta \leq 65^{\circ}$ 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 $\mathrm{Pb}, \mathrm{Cu}$ 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 $F_{o}>3 \sigma\left(F_{o}\right)$. The scattering factors for $\mathrm{Pb}, \mathrm{Cu}, \mathrm{As}, \mathrm{O}$ 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 $1 / \sigma^{2}\left(F_{o}\right)$, where $\sigma\left(F_{o}\right)$ 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 $0 \cdot 055$. 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

[^0]Table 2. Bayldonite, $(\mathrm{Cu}, \mathrm{Zn})_{3} \mathrm{~Pb}\left(\mathrm{AsO}_{4}\right)_{2}(\mathrm{OH})_{2}$ : atomic positional and thermal parameters, with standard deviations in parentheses

|  | $x$ | $y$ | $z$ | $B_{\mathrm{cu}}\left(\mathrm{A}^{2}\right)^{*}$ |
| :--- | :--- | :--- | :--- | :--- |
|  | r |  |  |  |
| $\mathrm{Cu}(1)$ | 0.0000 | 0.0000 | 0.0000 | $0.66(3)$ |
| $\mathrm{Cu}(2)$ | 0.5000 | 0.0000 | 0.0000 | $0.55(3)$ |
| $\mathrm{Cu}(3)$ | 0.2500 | 0.2500 | 0.5000 | $0.58(3)$ |
| Pb | 0.0000 | $0.2698(2)$ | 0.2500 | $1.19(2)$ |
| As | $0.2974(1)$ | $0.2164(2)$ | $0.1405(1)$ | $0.40(2)$ |
| $\mathrm{O}(1)$ | $0.3672(8)$ | $0.4590(14)$ | $0.1179(7)$ | $0.70(12)$ |
| $\mathrm{O}(2)$ | $0.1419(8)$ | $0.4986(14)$ | $0.4174(7)$ | $0.69(12)$ |
| $\mathrm{O}(3)$ | $0.1215(8)$ | $0.2212(15)$ | $0.0971(6)$ | $0.96(12)$ |
| $\mathrm{O}(4)$ | $0.3413(11)$ | $0.1260(15)$ | $0.2578(6)$ | $1.40(16)$ |
| $\mathrm{OH})$ | $0.3960(8)$ | $0.2487(12)$ | $0.4373(5)$ | $0.39(9)$ |
| 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 $\mathrm{Pb}-\mathrm{O}, \mathrm{Cu}-\mathrm{O}$ and $\mathrm{As}-\mathrm{O}$ bond lengths are $0.008 \AA$, and those in $\mathrm{O}-\mathrm{Pb}-\mathrm{O}, \mathrm{O}-\mathrm{Cu}-\mathrm{O}$ and $\mathrm{O}-\mathrm{As}-\mathrm{O}$ angles, $0 \cdot 2,0.3$ and $0.4^{\circ}$ 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

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


Fig. 1. Stereoscopic view of the bayldonite $(\mathrm{Cu}, \mathrm{Zn})_{3} \mathrm{~Pb}\left(\mathrm{AsO}_{4}\right)_{2}-$ $(\mathrm{OH})_{2}$ structure. Note the alternating Cu octahedral sheet and the Pb -arsenate sheet along the $c$ axis.

Table 3. Bayldonite, $(\mathrm{Cu}, \mathrm{Zn})_{3} \mathrm{~Pb}\left(\mathrm{AsO}_{4}\right)_{2}(\mathrm{OH})_{2}$ : interatomic distances ( $\AA$ ) and angles $\left({ }^{\circ}\right)$, with standard deviations in parentheses

The $\mathrm{Cu}(1)$ octahedron

| $\mathrm{Cu}(1)-\mathrm{O}(1)$ | $2.423(10)(\times 2)$ |
| :--- | :--- |
| $\mathrm{Cu}(1)-\mathrm{O}(3)$ | $2.039(8)(\times 2)$ |
| $\mathrm{Cu}(1)-(\mathrm{OH})$ | $1.891(7)(\times 2)$ |
| Mean | $2 \cdot 118$ |
|  |  |
| $\mathrm{O}(1)-\mathrm{O}(3)$ | $3.09(1)(\times 2)$ |
| $\mathrm{O}(1)-(\mathrm{OH})$ | $3 \cdot 15(1)(\times 2)$ |
| $\mathrm{O}(1)-\mathrm{O}\left(3^{\prime}\right)$ | $3.24(1)(\times 2)$ |
| $\mathrm{O}(1)-(\mathrm{OH})^{\prime}$ | $3.08(1)(\times 2)$ |
| $\mathrm{O}(3)-(\mathrm{OH})$ | $2.74(1)(\times 2)$ |
| $\mathrm{O}(3)-(\mathrm{OH})^{\prime}$ | $2.83(1)(\times 2)$ |

The $\mathrm{Cu}(2)$ octahedron

| $\mathrm{Cu}(2)-\mathrm{O}(3)$ | $2.272(9)(\times 2)$ |
| :--- | :--- |
| $\mathrm{Cu}(2)-\mathrm{O}(2)$ | $2.087(10)(\times 2)$ |
| $\mathrm{Cu}(2)-(\mathrm{OH})$ | $1.878(7)(\times 2)$ |
| Mean | 2.079 |
|  |  |
| $\mathrm{O}(3)-\mathrm{O}(2)$ | $3.09(1)(\times 2)$ |
| $\mathrm{O}(3)-(\mathrm{OH})$ | $2.74(1)(\times 2)$ |
| $\mathrm{O}(3)-\mathrm{O}\left(2^{\prime}\right)$ | $3.08(1)(\times 2)$ |
| $\mathrm{O}(3)-(\mathrm{OH})^{\prime}$ | $3.15(1)(\times 2)$ |
| $\mathrm{O}(2)-(\mathrm{OH})$ | $2.63(1)(\times 2)$ |
| $\mathrm{O}(2)-(\mathrm{OH})^{\prime}$ | $2.98(1)(\times 2)$ |

The Cu(3) octahedron

| $\mathrm{Cu}(3)-\mathrm{O}(1)$ | $2.454(8)(\times 2)$ |
| :--- | :--- |
| $\mathrm{Cu}(3)-\mathrm{O}(2)$ | $2.000(8)(\times 2)$ |
| $\mathrm{Cu}(3)-(\mathrm{OH})$ | $1.924(9)(\times 2)$ |
| Mean | 2.126 |
|  |  |
| $\mathrm{O}(1)-\mathrm{O}(2)$ | $3.11(1)(\times 2)$ |
| $\mathrm{O}(1)-(\mathrm{OH})$ | $3.08(1)(\times 2)$ |
| $\mathrm{O}(1)-\mathrm{O}\left(2^{\prime}\right)$ | $3.22(1)(\times 2)$ |
| $\mathrm{O}(1)-(\mathrm{OH})^{\prime}$ | $3.15(1)(\times 2)$ |
| $\mathrm{O}(2)-(\mathrm{OH})$ | $2.98(1)(\times 2)$ |
| $\mathrm{O}(2)-(\mathrm{OH})^{\prime}$ | $2.92(1)(\times 2)$ |

The Pb polyhedron

| $\mathrm{Pb}-\mathrm{O}(1)$ | $2 \cdot 693(8)(\times 2)$ |
| :--- | :--- |
| $\mathrm{Pb}-\mathrm{O}(2)$ | $2 \cdot 752(9)(\times 2)$ |
| $\mathrm{Pb}-\mathrm{O}(3)$ | $2 \cdot 776(9)(\times 2)$ |
| $\mathrm{Pb}-\mathrm{O}(4)$ | $2 \cdot 668(10)(\times 2)$ |
| Mean | $2 \cdot 722$ |
|  |  |
| $\mathrm{O}(1)-\mathrm{O}(2)$ | $3 \cdot 22(1)(\times 2)$ |
| $\mathrm{O}(1)-\mathrm{O}(3)$ | $4 \cdot 27(1)(\times 2)$ |
| $\mathrm{O}(1)-(4)$ | $4 \cdot 44(1)(\times 2)$ |
| $\mathrm{O}(2)-\mathrm{O}(3)$ | $4 \cdot 75(1)(\times 2)$ |
| $\mathrm{O}(2)-\mathrm{O}(4)$ | $2 \cdot 63(1)(\times 2)$ |
| $\mathrm{O}(3)-\mathrm{O}(4)$ | $3 \cdot 10(1)(\times 2)$ |
| $\mathrm{O}\left(1^{\prime}\right)-\mathrm{O}(2)$ | $5 \cdot 40(1)(\times 2)$ |
| $\mathrm{O}\left(1^{\prime}\right)-\mathrm{O}(3)$ | $3.09(1)(\times 2)$ |
| $\mathrm{O}\left(1^{\prime}\right)-\mathrm{O}(4)$ | $4 \cdot 14(1)(\times 2)$ |
| $\mathrm{O}\left(2^{\prime}\right)-\mathrm{O}(3)$ | $3.08(1)(\times 2)$ |
| $\mathrm{O}\left(2^{\prime}\right)-\mathrm{O}(4)$ | $3 \cdot 34(1)(\times 2)$ |
| $\mathrm{O}\left(3^{\prime}\right)-\mathrm{O}(4)$ | $4.74(1)(\times 2)$ |
| $\mathrm{O}(4)-\mathrm{O}\left(4^{\prime}\right)$ | $3.95(1)(\times 2)$ |
| $\mathrm{O}(2)-\mathrm{O}\left(2^{\prime}\right)$ | $4.80(1)(\times 2)$ |
| $\mathrm{O}(3)-\mathrm{O}\left(3^{\prime}\right)$ | $5.52(1)(\times 2)$ |
| $\mathrm{O}(4)-\mathrm{O}\left(4^{\prime}\right)$ | $3.29(1)(\times 2)$ |

$\mathrm{O}(1)-\mathrm{Cu}(1)-\mathrm{O}(3) \quad 87.2(3)(\times 2)$
$\mathrm{O}(1)-\mathrm{Cu}(1)-(\mathrm{OH}) \quad 93.1(3)(\times 2)$ $\mathrm{O}(1)-\mathrm{Cu}(1)-\mathrm{O}\left(3^{\prime}\right) \quad 92.8(3)(\times 2)$ $\mathrm{O}(1)-\mathrm{Cu}(1)-(\mathrm{OH})^{\prime} \quad 86.9(3)(\times 2)$ $\mathrm{O}(3)-\mathrm{Cu}(1)-(\mathrm{OH}) \quad 88.2(3)(\times 2)$ $\mathrm{O}(3)-\mathrm{Cu}(1)-(\mathrm{OH})^{\prime} \quad 91.9(3)(\times 2)$ Mean $90 \cdot 0$

| $\mathrm{O}(3)-\mathrm{Cu}(2)-\mathrm{O}(2)$ | $90.3(3)(\times 2)$ |
| :--- | :--- |
| $\mathrm{O}(3)-\mathrm{Cu}(2)-(\mathrm{OH})$ | $81.9(3)(\times 2)$ |
| $\mathrm{O}(3)-\mathrm{Cu}(2)-\mathrm{O}(2)^{\prime}$ | $89.7(3)(\times 2)$ |
| $\mathrm{O}(3)-\mathrm{Cu}(2)-(\mathrm{OH})^{\prime}$ | $98.1(3)(\times 2)$ |
| $\mathrm{O}(2)-\mathrm{Cu}(2)-(\mathrm{OH})$ | $82.8(3)(\times 2)$ |
| $\mathrm{O}(2)-\mathrm{Cu}(2)-(\mathrm{OH})^{\prime}$ | $97.2(3)(\times 2)$ |
| Mean |  |


| $\mathrm{O}(1)-\mathrm{Cu}(3)-\mathrm{O}(2)$ | $88.1(3)(\times 2)$ |
| :--- | :--- |
| $\mathrm{O}(1)-\mathrm{Cu}(3)-(\mathrm{OH})$ | $88.7(3)(\times 2)$ |
| $\mathrm{O}(1)-\mathrm{Cu}(3)-\mathrm{O}(2)^{\prime}$ | $91.9(3)(\times 2)$ |
| $\mathrm{O}(1)-\mathrm{Cu}(3)-(\mathrm{OH})^{\prime}$ | $91.3(3)(\times 2)$ |
| $\mathrm{O}(2)-\mathrm{Cu}(3)-(\mathrm{OH})$ | $96.0(3)(\times 2)$ |
| $\mathrm{O}(2)-\mathrm{Cu}(3)-(\mathrm{OH})^{\prime}$ | $84.0(3)(\times 2)$ |
| Mean | 90.0 |

$\mathrm{O}(1)-\mathrm{Pb}-\mathrm{O}(2)$
$\mathrm{O}(1)-\mathrm{Pb}-\mathrm{O}(3)$
$\mathrm{O}(1)-\mathrm{Pb}-\mathrm{O}(4)$
$\mathrm{O}(2)-\mathrm{Pb}-\mathrm{O}(3)$
$\mathrm{O}(2)-\mathrm{Pb}-\mathrm{O}(4)$ $\mathrm{O}(3)-\mathrm{Pb}-\mathrm{O}(4)$
$\mathrm{O}\left(1^{\prime}\right)-\mathrm{Pb}-\mathrm{O}(2)$
$\mathrm{O}\left(1^{\prime}\right)-\mathrm{Pb}-\mathrm{O}(3)$
$\mathrm{O}\left(1^{\prime}\right)-\mathrm{Pb}-\mathrm{O}(4)$
$\mathrm{O}\left(2^{\prime}\right)-\mathrm{Pb}-\mathrm{O}(3)$
$\mathrm{O}\left(2^{\prime}\right)-\mathrm{Pb}-\mathrm{O}(4)$
$\mathrm{O}\left(3^{\prime}\right)-\mathrm{Pb}-\mathrm{O}(4)$
$\mathrm{O}(1)-\mathrm{Pb}-\mathrm{O}\left(1^{\prime}\right)$
$\mathrm{O}(2)-\mathrm{Pb}-\mathrm{O}\left(2^{\prime}\right)$
$\mathrm{O}(3)-\mathrm{Pb}-\mathrm{O}\left(3^{\prime}\right)$
$\mathrm{O}(4)-\mathrm{Pb}-\mathrm{O}\left(4^{\prime}\right)$
$\mathrm{O}(\mathrm{OH})$ and $\left.\mathrm{O}\left(3^{\prime}\right)-\mathrm{O}(\mathrm{OH})^{\prime}\right]$. These chains are crosslinked through the $\mathrm{Cu}(3)$ octahedra, which share opposite octahedral edges $\left[\mathrm{O}(1)-\mathrm{O}(\mathrm{OH})\right.$ and $\mathrm{O}\left(1^{\prime}\right)-$ $\left.\mathrm{O}(\mathrm{OH})^{\prime}\right]$ with two $\mathrm{Cu}(1)$ 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 $\left\|\mathrm{AsO}_{4}\right\|$ tetrahedron |  |  |  |
| :---: | :---: | :---: | :---: |
| As-O(1) | 1.666 (8) | $\mathrm{O}(1)-\mathrm{As}-\mathrm{O}(2)$ | 108.8 (4) |
| $\mathrm{As}-\mathrm{O}(2)$ | 1.724 (8) | $\mathrm{O}(1)-\mathrm{As}-\mathrm{O}(3)$ | 111.9 (4) |
| $\mathrm{As}-\mathrm{O}(3)$ | 1.719 (8) | $\mathrm{O}(1)-\mathrm{As}-\mathrm{O}(4)$ | 116.8 (5) |
| $\mathrm{As}-\mathrm{O}(4)$ | 1.674 (8) | $\mathrm{O}(2)-\mathrm{As}-\mathrm{O}(3)$ | 108.4 (4) |
| Mean | 1.696 | $\mathrm{O}(2)-\mathrm{As}-\mathrm{O}(4)$ | 101.4 (4) |
|  |  | $\mathrm{O}(3)-\mathrm{As}-\mathrm{O}(4)$ | 108.8 (5) |
| $\mathrm{O}(1)-\mathrm{O}(2)$ | 2.76 (1) | Mean | 109.4 |
| $\mathrm{O}(1)-\mathrm{O}(3)$ | 2.80 (1) |  |  |
| $\mathrm{O}(1)-\mathrm{O}(4)$ | 2.85 (1) |  |  |
| $\mathrm{O}(2)-\mathrm{O}(3)$ | 2.79 (1) |  |  |
| $\mathrm{O}(2)-\mathrm{O}(4)$ | 2.63 (1) |  |  |
| $\mathrm{O}(3)-\mathrm{O}(4)$ | 2.76 (1) |  |  |
| Hydrogen bonds |  |  |  |
| (OH)- H | 1.41 (18) | $(\mathrm{OH})-\mathrm{H}-\mathrm{O}(4)$ | 139 (14) |
| $\mathrm{O}(4)-\mathrm{H}$ | 1.30 (18) | $\mathrm{Cu}(1)-(\mathrm{OH})-\mathrm{H}$ | 140 (7) |
| $(\mathrm{OH})-\mathrm{O}(4)$ | $2 \cdot 54$ (1) | $\mathrm{Cu}(2)-(\mathrm{OH})-\mathrm{H}$ | 82 (7) |
|  |  | $\mathrm{Cu}(3)-(\mathrm{OH})-\mathrm{H}$ | 117 (7) |
| Cation-cation distances ( $<3.5 \AA$ ) |  |  |  |
| $\mathrm{Cu}(1)-\mathrm{Cu}(2)$ | 2.9485 (5) | As-Cu(1) | $3 \cdot 3685$ (10) |
| $\mathrm{Cu}(1)-\mathrm{Cu}(3)$ | 2.9341 (5) | $\mathrm{As}-\mathrm{Cu}(2)$ | 3.4681 (10) |
| $\mathrm{Cu}(2)-\mathrm{Cu}(3)$ | 2.9341 (5) | As-Cu(3) | 3.3446 (10) |
|  |  | $\mathrm{Pb}-\mathrm{As}$ | 3.4332 (11) |

Alternatively, the octahedral sheet can be considered as a distorted version of the hydrargillite, $\mathrm{Al}(\mathrm{OH})_{3}$ type sheet. A comparable open octahedral sheet structure has been found in veszelyite, $(\mathrm{Cu}, \mathrm{Zn})_{2} \mathrm{Zn}\left(\mathrm{PO}_{4}\right) \cdot 2 \mathrm{H}_{2} \mathrm{O}$ (Ghose, Leo \& Wan, 1974), which contains eightmembered octahedral rings.

## (b) The lead arsenate sheet

Pb is coordinated by eight O atoms, the $\mathrm{PbO}_{8}$ polyhedron being a square antiprism (Fig. 3). Alternating $\mathrm{PbO}_{8}$ 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 ( $\sim 2 \AA$ ) 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 $\mathrm{Cu}(1)$ and $\mathrm{Cu}(2)$ octahedra form a chain parallel to the $b$ axis; the arsenate tetrahedra share two corners with two adjacent $\mathrm{Cu}(1)$ and $\mathrm{Cu}(2)$ octahedra, such that an edge of the $\mathrm{AsO}_{4}$ tetrahedron is parallel to the $b$ axis. The periodicity of this $\mathrm{Cu}-$ arsenate chain in bayldonite is $5.893 \AA$ (Fig. 5). Topologically similar Cu -phosphate, Cu -arsenate and Cu -sulfate chains are present in the structures of tsumebite $\mathrm{Pb}_{2} \mathrm{Cu}\left[\mathrm{PO}_{4} \mathrm{SO}_{4} \mathrm{OH}\right]$ (Nicholls, 1966), Astsumebite $\mathrm{Pb}_{2} \mathrm{Cu}\left[\mathrm{AsO}_{4} \mathrm{SO}_{4}(\mathrm{OH})\right]$, fornacite $\mathrm{Pb}_{2} \mathrm{Cu}-$ $\left[\mathrm{AsO}_{4} \mathrm{CrO}_{4}(\mathrm{OH})\right]$ (Cocco, Fanfani \& Zanazzi, 1967), vauquelinite $\mathrm{Pb}_{2} \mathrm{Cu} \mid \mathrm{PO}_{4} \mathrm{CrO}_{4}(\mathrm{OH})$ (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 $\mathrm{PbCuSO}_{4}(\mathrm{OH})_{2}$ (Bachmann \& Zemann, 1961). All these minerals are characterized by $b$ dimensions which range from 5.65 (linarite) to $5.92 \AA$ (As-tsumebite).

## Stereochemistry of the cupric ions and copper-zinc substitution

All the three independent $\mathrm{Cu}^{2+}$ ions, occurring in special positions with point symmetry $\overline{1}$, show the usual Jahn-Teller distortion. Each tetragonally distorted $\left[\mathrm{CuO}_{4}(\mathrm{OH})_{2}\right]$ 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, $\mathrm{Cu}-(\mathrm{OH})$ distances (average $1.898 \AA$ ) are significantly shorter than the $\mathrm{Cu}-\mathrm{O}$ distances (average 2.042 $\AA$ ). The square-planar $\mathrm{Cu}-\mathrm{O}$ (or OH ) distances show little variation, with an average of $1.970 \AA$. In contrast, the apical $\mathrm{Cu}-\mathrm{O}$ distances vary from 2.272 for $\mathrm{Cu}(2)$ to 2.423 for $\mathrm{Cu}(1)$ and $2.454 \AA$ for $\mathrm{Cu}(3)$. Hence, the $\mathrm{Cu}(3)$ octahedron is the most and the $\mathrm{Cu}(2)$ octahedron the least distorted in terms of bond distances.

The chemical analysis of the bayldonite sample from Tsumeb indicates $1 \cdot 1 \mathrm{wt} \% \mathrm{ZnO}$ (Cesbron \& Vachey, 1974). Since the octahedral coordination for $\mathrm{Zn}^{2+}$ (a $d^{10}$ ion) is expected to be regular, $\mathrm{Cu}(2)$ is the most likely site for Zn substitution. In fact, the $\mathrm{Cu}(2)$ coordination in bayldonite is closely comparable to the octahedral $\left[\mathrm{ZnO}_{4}(\mathrm{OH})_{2}\right]$ coordination in adamite, $\mathrm{Zn}_{2} \mathrm{AsO}_{4}(\mathrm{OH})$, where the $\mathrm{Zn}-\mathrm{O}$ distances are 2.051 $(\times 2), 2.062(\times 2)$ and $2.261 \AA(\times 2)$ (average $2.125 \AA$ ) (Hill, 1976; Hawthorne, 1976). Crystal-chemically it seems possible that bayldonite, richer in Zn , may attain a composition of $\mathrm{PbCu}_{2} \mathrm{Zn}\left(\mathrm{AsO}_{4}\right)_{2}(\mathrm{OH})_{2}$.


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

## The tetrahedral $\left[\mathrm{AsO}_{4}\right]$ ion

The tetrahedral $\left[\mathrm{AsO}_{4}\right]$ group, with an average As-O distance of $1.696 \AA$ shows considerable variation in As-O bond lengths (from 1.666 to 1.724 $\AA$ ) and $\mathrm{O}-\mathrm{As}-\mathrm{O}$ angles (from $101 \cdot 4$ to $116 \cdot 8^{\circ}$ ). One of the two short As-O bonds involves $\mathrm{O}(4)$, 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, $\mathrm{O}(1)$ is involved in two long $\mathrm{Cu}-\mathrm{O}$ bonds, in addition to a $\mathrm{Pb}-\mathrm{O}$ bond. In contrast, $\mathrm{O}(2)$ is involved in two short $\mathrm{Cu}-\mathrm{O}$ bonds and a $\mathrm{Pb}-\mathrm{O}$ bond, whereas $\mathrm{O}(3)$ is involved in one short and one long $\mathrm{Cu}-\mathrm{O}$ bond and a $\mathrm{Pb}-\mathrm{O}$ bond. Hence, the As-O(1) bond ( $1.666 \AA$ ) is significantly shorter than the As-O(2) (1.723 £) and As-O(3) ( $1.719 \AA$ ) bonds. In effect, the variation of the As-O bond lengths reflects the variable charges the O atoms are receiving from other cations.

## $\mathrm{PbO}_{8}$ polyhedron

The $\mathrm{PbO}_{8}$ 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, $\mathrm{PbSbO}_{2} \mathrm{Cl}$ (Giuseppetti \& Tadini, 1973), $\mathrm{PbTiO}_{3}$ (Shirane, Pepinsky \& Frazer, 1956), and diaboleite $\mathrm{Pb}_{2} \mathrm{Cu}(\mathrm{OH})_{4} \mathrm{Cl}_{2}$ (Rouse, 1971). In bayldonite, all $\mathrm{Pb}-\mathrm{O}$ bonds are ionic, since all the $\mathrm{Pb}-\mathrm{O}$ distances (average $2.722 \AA$ ) are larger than the sum of the ionic radii of $\mathrm{Pb}^{2+}$ and $\mathrm{O}^{2-}(2 \cdot 69 \AA)$ (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 $\mathrm{O}(4)$ and the OH group, the $(\mathrm{OH})-\mathrm{H}$ and $\mathrm{O}(4)-\mathrm{H}$ distances being 1.4 and $1.3 \AA$ 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 $\mathrm{Pb}-\mathrm{O}$ bonds, one $\mathrm{As}-\mathrm{O}$ 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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[^0]:    * 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.

