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THE CRYSTAL STRUCTURE OF KEYITE, $Cu_3^{2+}(Zn,Cu^{2+})_4Cd_2(AsO_4)_6(H_2O)_2$, AN OXYSALT MINERAL WITH ESSENTIAL CADMIUM

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ABSTRACT

The crystal structure of keyite, $Cu_3^{2+}(Zn,Cu^{2+})_4Cd_2(AsO_4)_6(H_2O)_2$, *a* 11.654(3), *b* 12.780(5), *c* 6.840(3) Å, β 99.11(3)°, *V* 1005.8(6) Å^3, *I*2/*a*, *Z* = 2, was solved by direct methods and refined to an *R* index of 9.3% based on 1123 observed reflections measured with Mo*K*α X-radiation. There are two Cu^{2+} sites; *Cu*(1) is octahedrally coordinated by four oxygen atoms and two H_2O groups, and is exactly half-occupied by Cu^{2+}; *Cu*(2) is coordinated by four oxygen atoms in a square-planar arrangement. There is one *Zn* site, occupied by Zn and minor Cu^{2+}, and octahedrally coordinated by six oxygen atoms. There is one *Cd* site occupied dominantly by Cd^{2+} and coordinated by six oxygen atoms in a trigonal prismatic arrangement. There are two *As* sites, both occupied by As^{5+} and tetrahedrally coordinated by oxygen atoms. The *Cu*(1)ϕ_6 (ϕ: unspecified ligand) octahedra share corners to form a [$Cu\phi_5$] chain in which only alternate octahedra are occupied. This chain is flanked by AsO_4 tetrahedra and CdO_6 polyhedra to form a heteropolyhedral ribbon that extends along the *c* axis. These ribbons are cross-linked by CuO_4 groups into a sheet parallel to (100). These sheets alternate with parallel sheets of [Zn_2O_{10}] octahedral dimers and AsO_4 tetrahedra to form a very complex heteropolyhedral framework. The formula of keyite is extensively revised from the original description, but the revised formula agrees closely with the results of original chemical analysis and of electron-microprobe analyses obtained as part of this work. The new formula shows that keyite contains essential Cd.

Keywords: keyite, crystal structure, arsenate, copper oxysalt, cadmium.

SOMMAIRE

Nous avons résolu et affiné la structure cristalline de la keyite, $Cu_3^{2+}(Zn,Cu^{2+})_4Cd_2(AsO_4)_6(H_2O)_2$, *a* 11.654(3), *b* 12.780(5), *c* 6.840(3) Å, β 99.11(3)°, *V* 1005.8(6) Å^3, *I*2/*a*, *Z* = 2, par méthodes directes jusqu'à un résidu *R* de 9.3% en utilisant 1123 réflexions observées et mesurées avec rayonnement Mo*K*α. Il y a deux sites Cu^{2+}; *Cu*(1) possède une coordinence six (quatre atomes d'oxygène et deux groupes H_2O), avec la moitié de ceux-ci seulement contenant un atome Cu^{2+}. Le site *Cu*(2) est coordonné à quatre atomes d'oxygène dans un agencement en plan carré. La structure contient un site *Zn*, contenant du Zn et un peu de Cu^{2+}, et coordonné par six atomes d'oxygène. Elle contient aussi un site *Cd* rempli surtout de Cd^{2+} et coordonné par six atomes d'oxygène en agencement prismatique trigonal. Il y a quatre sites *As*, chacun contenant un atome de As^{5+} en coordinence tétraédrique avec des atomes d'oxygène. Les octaèdres *Cu*(1)ϕ_6 (ϕ: ligand non spécifié) partagent des coins pour donner une chaîne [$Cu\phi_5$] dans laquelle chaque deuxième octaèdre seulement est rempli. Cette chaîne est décorée par des tétraèdres AsO_4 et des polyèdres CdO_6 latéraux pour former un ruban hétéropolyédrique qui longe l'axe *c*. Ces rubans sont liés par des groupes CuO_4 pour former un feuillet parallèle à (100). Ces feuillets alternent avec des feuillets parallèles de dimères d'octaèdres [Zn_2O_{10}] et de tétraèdres AsO_4 et forment une trame hétéropolyédrique très complexe. La formule de la keyite est fondamentalement différente de celle qui avait antérieurement été proposée, quoiqu'elle concorde étroitement avec les résultats de l'analyse chimique dans la littérature et de nos analyses à la microsonde électronique. La nouvelle formule démontre que la présence du cadmium est essentielle.

(Traduit par la Rédaction)

Mots-clés: keyite, structure cristalline, arsenate, oxysel de cuivre, cadmium.

INTRODUCTION

Keyite is a complex copper – zinc – cadmium arsenate described from Tsumeb, Namibia, by Embrey *et al.* (1977). It occurs as small blue prisms in cavities in tennantite ore, associated with cuprodamite and schultenite. As part of our interest in copper oxysalt minerals, we have solved and refined the crystal structure of keyite, and present the results here.

EXPERIMENTAL

Crystals of keyite are prismatic [001] to tabular {010}, commonly tapering or showing subparallel intergrowth on {010} (Embrey *et al.* 1977). Most crystals of keyite diffract extremely poorly, and "split" or multiple reflections are the rule. We have examined at least a dozen samples, mainly purchased from dealers, without success over the last ten years. Finally,

TABLE 1. MISCELLANEOUS INFORMATION FOR KEYITE

a (Å)	11.654(3)	Crystal size (mm)	0.130 x 0.032 x 0.020
b	12.780(5)	radiation	Mo*K*α/Gr
c	6.840(3)	No. of intensities	1481
β (°)	99.11(3)	No. of $\lvert F_o\rvert > 5\sigma(\lvert F_o\rvert)$	1123
V (Å³)	1005.8(6)	min. transmission	0.412
Sp. Gr.	*I*2/*a*	max. transmission	0.710
Z	2	*R*(obs) %	9.3
D$_c$ (g/cm^{-3})	5.106	*wR*(obs) %	11.4

Cell content: $2[Cu_3^{2+}(Zn,Cu^{2+})_4Cd_2(AsO_4)_6(H_2O)_2]$
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$
$wR = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma F_o^2]^{½}$, $w = 1$

we were provided with an exceptional sample by Mr. William Pinch, and eventually found a minute acicular fragment (Table 1) that gave a usable diffraction-pattern. The crystal showed detectable divergence of the faces of the {010} form that defines the principal tabular habit. This divergence indicates that the crystal is not a true single crystal, but a subparallel aggregate, which accounts for the peak asymmetry and varying peak-maxima positions on psi-scans. However, there isn't that much more keyite in the world to look at, and so we decided to collect data on this crystal.

The crystal was mounted on a Siemens *P*4 automated four-circle diffractometer and aligned on twenty-six relatively intense reflections; we note here that several intense reflections could not be used for orientation owing to asymmetry. The orientation matrix and cell dimensions (Table 1) were determined from the setting angles by least-squares refinement. We collected 1481 unique reflections out to 60° 2θ ($\overline{16} \le h \le 16$, $\overline{18} \le k \le 0$, $0 \le l \le 9$) with scan speeds between 1.50 and 14.65° 2θ/min and using a broad scan-range. We collected psi-scan intensities, but had problems with shifting peak-maxima, and both thin-plate and ellipsoidal corrections gave poor results. We corrected for absorption by Gaussian quadrature integration, corrected for Lorentz, polarization and background effects, and reduced the intensities to structure factors; of the 1481 unique reflections, 1123 were considered as observed ($\lvert F_o\rvert > 5\sigma\lvert F_o\rvert$).

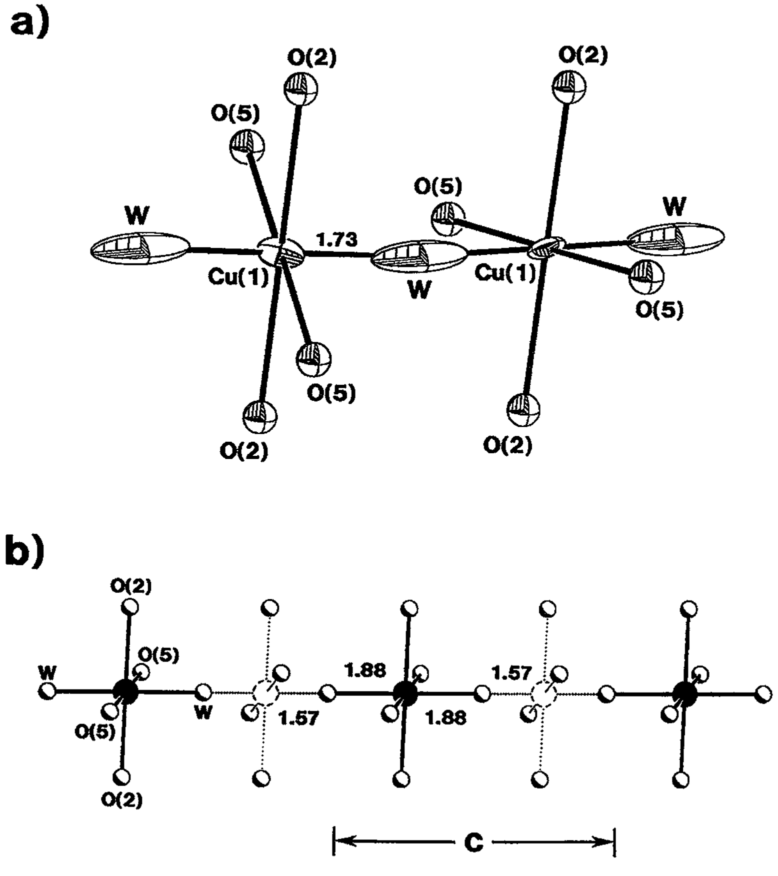

FIG. 1. Details of the *Cu*(1) site and its coordination: (a) adjacent *Cu*(1) sites, each coordinated by four O anions and two H_2O (= *W*) groups; note the very anisotropic displacement of the *W* groups and the anomalously short *Cu*(1)–*W* distance of 1.73 Å; this is an oblique view, tilted to minimize atom overlap; (b) ordered interpretation of a split-site model of the *W* site whereby *Cu*(1) sites are alternately occupied (black circles) and vacant (broken unshaded circles); this view is projected from [010].

TABLE 2. FINAL PARAMETERS FOR KEYITE

Site	x	y	z	$^{+}U_{eq}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	3/4	1/4	1/4	162(25)	76(34)	156(45)	254(46)	−83(34)	24(32)	52(29)
Cu(2)	1/4	0.2402(3)	0	134(12)	48(16)	68(18)	278(24)	0	0(15)	0
Zn	0.5246(2)	0.0928(2)	0.1583(5)	113(7)	55(11)	49(11)	234(15)	−12(10)	19(10)	1(9)
Cd	3/4	0.4964(2)	0	139(9)	38(12)	93(14)	274(18)	0	−8(10)	0
As(1)	1/4	0.0277(3)	0	104(9)	30(12)	64(14)	222(18)	0	36(12)	0
As(2)	0.5057(2)	0.3638(2)	0.1414(4)	91(6)	34(9)	34(9)	204(12)	−13(9)	14(8)	−3(8)
O(1)	0.975(1)	0.065(1)	0.147(2)	102(30)						
O(2)	0.570(1)	0.246(1)	0.188(3)	134(33)						
O(3)	0.350(2)	0.122(1)	0.090(3)	145(33)						
O(4)	0.931(1)	0.419(1)	0.041(3)	118(31)						
O(5)	0.708(2)	0.045(1)	0.184(3)	151(34)						
O(6)	0.362(1)	0.350(1)	0.063(3)	122(32)						
W	3/4	0.268(2)	0.023(5)	120*						

$^{+}$ $U = U \times 10^4$ * fixed during refinement

STRUCTURE SOLUTION AND REFINEMENT

All calculations were done with the SHELXTL PC Plus system of programs; R and wR indices are of the conventional form and are given as percentages. The structure was solved by direct methods. The E statistics indicate that the structure is centrosymmetric, and systematic absences indicate the presence of an a glide for the I-centered cell originally assigned by Embrey *et al.* (1977). The solution with the highest combined figure-of-merit in the space group $I2/a$ proved to be correct, and the structure was refined by a combination of least-squares refinement and difference-Fourier synthesis to an R index of 9.3%; we consider this value satisfactory in view of the poorly diffracting nature of the material. Site occupancies were assigned on the basis of site-scattering refinement and the unit formula reported by Embrey *et al.* (1977). One anion position, designated W, showed extremely anisotropic displacements (Fig. 1a), and was modeled by splitting the atom into two half-occupied sites. Final atomic parameters are listed in Table 2, and selected interatomic distances and angles are given in Table 3. A bond-valence table, calculated from the parameters of Brown & Altermatt (1985), is shown as Table 4. Observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

DESCRIPTION OF THE STRUCTURE

Cation coordination

There are two sites, labeled *Cu*(1) and *Cu*(2), and Cu^{2+} was assigned to these sites on the basis of the observed coordination-geometry. The *Cu*(1) site is surrounded by four oxygen atoms and two H_2O groups in an octahedral arrangement. As noted above and in Figure 1a, the H_2O group, designated W, showed a very anisotropic displacement and was modeled in the last stages of refinement as two half-occupied sites with a separation of 0.31 Å. Site-scattering refinement showed that the *Cu*(1) site is actually half-occupied by Cu, and it seems reasonable to associate this half-occupancy with the split-site disorder of the W anion. A single-site model for W gives a *Cu*(1)–W distance of 1.73 Å, a value that is beyond the range of observed *Cu*–ϕ distances (Eby & Hawthorne 1993, Burns & Hawthorne 1995). On the other hand, a split-site model for W produces *Cu*(1)–W distances of 1.57 and 1.88 Å. The former value is much too short for a *Cu*–ϕ distance; the latter value is somewhat short for a *Cu*–ϕ distance, but is close to the lower range of observed values. Thus we interpret the value 1.88 Å to be associated with an occupied *Cu*(1) site, and the value 1.53 Å to be associated with a vacant *Cu*(1) site. The *Cu*(1)ϕ_6 octahedra form a corner-sharing $[M\phi_5]$ chain (M: unspecified cation, ϕ: unspecified anion) extending parallel to the c axis, and we propose that this chain has alternating occupied and vacant *Cu*(1) sites, as shown in Figure 1b. This pattern of order has the potential to double the length of the c dimension. However, it does *not* do this, as chains adjacent in the X and Y directions are not directly coupled, and hence are disordered relative to each other. The *Cu*(1)–O distances show the typical Jahn–Teller distortion of $Cu\phi_6$ octahedra, with four short (~1.98 Å) and two long (2.69 Å) bonds.

The *Cu*(2) site is surrounded by four oxygen anions in a square-planar arrangement. The observed <*Cu*(2)–ϕ> distance of 1.94 Å is typical for this arrangement (Burns & Hawthorne 1995), and the incident bond-valence sum at the central *Cu*(2) is equal to the ideal value of 2.0 valence units (*vu*).

There is one *Zn* site, occupied primarily by Zn but with some Cu. This site is surrounded by six oxygen atoms between 2.03 and 2.20 Å, and with a <*Zn*–O> distance of 2.09 Å; the latter value is in accord with the assignment of Zn and Cu to this site, as is the observed X-ray scattering.

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

Cu(1)–O(2),a	2.07(2)	x2	Cd–O(4),b	2.31(2)	x2
Cu(1)–O(5),a	2.69(2)	x2	Cd–O(5)a,f	2.21(2)	x2
Cu(1)–Wi,j	1.88(4)	x2	Cd–O(6)g,h	2.36(2)	x2
<Cu(1)–O>	2.21		<Cd–O>	2.29	
<Cu(1)–O_{eq}>	1.98				
Cu(2)–O(3),d	1.95(2)	x2	As(1)–O(3),d	1.72(2)	x2
Cu(2)–O(6),d	1.92(2)	x2	As(1)–O(5)c,e	1.70(2)	x2
<Cu(2)–O>	1.94		<As(1)–O>	1.71	
Zn–O(1)b	2.12(2)		As(2)–O(1)a	1.70(2)	
Zn–O(1)c	2.09(2)		As(2)–O(2)	1.69(2)	
Zn–O(2)	2.03(2)		As(2)–O(4)b	1.70(2)	
Zn–O(3)	2.05(2)		As(2)–O(6)	1.68(2)	
Zn–O(4)a	2.04(2)		<As(2)–O>	1.69	
Zn–O(5)	2.20(2)				
<Zn–O>	2.09				
Cu(1) octahedron					
Wi–O(2)	2.74(3)	x2	Wi–Cu(1)–O(2)	87.6(5)	
Wi–O(5)	3.25(4)	x2	Wi–Cu(1)–O(5)	89.0(9)	
Wj–O(2)	2.86(3)	x2	Wj–Cu(1)–O(2)	92.4(5)	
Wj–O(5)	3.31(4)	x2	Wj–Cu(1)–O(5)	91.0(9)	
O(2)–O(5)	3.03(3)	x2	O(2)–Cu(1)–O(5)	78.0(6)	
O(2)–O(5)a	3.72(4)	x2	O(2)–Cu(1)–O(5)a	102.0(6)	
<O–O>	3.15		<O–Cu(1)–O>	90.0	
Cu(2) square-planar group					
O(3)–O(3)d	2.46(3)		O(3)–Cu(2)–O(3)d	78(1)	
O(6)–O(6)d	2.62(3)		O(6)–Cu(2)–O(6)d	86(1)	
O(3)–O(6)	2.93(2)	x2	O(3)–Cu(2)–O(6)	98.2(7)	
<O–O>	2.74		<O–Cu(2)–O>	90.1	
Zn octahedron					
O(3)–O(2)	3.00(2)		O(3)–Zn–O(2)	94.8(7)	
O(3)–O(4)a	3.33(3)		O(3)–Zn–O(4)a	109.1(7)	
O(3)–O(1)c	2.79(2)		O(3)–Zn–O(1)c	84.8(7)	
O(3)–O(1)b	2.89(3)		O(3)–Zn–O(1)b	87.8(7)	
O(5)–O(2)	3.03(3)		O(5)–Zn–O(2)	91.3(7)	
O(5)–O(4)a	2.71(3)		O(5)–Zn–O(4)a	79.2(7)	
O(5)–O(1)c	3.03(2)		O(5)–Zn–O(1)c	89.7(7)	
O(5)–O(1)b	2.87(2)		O(5)–Zn–O(1)b	83.0(7)	
O(2)–O(4)a	2.81(3)		O(2)–Zn–O(4)a	87.0(7)	
O(4)a–O(1)c	2.91(2)		O(4)a–Zn–O(1)c	89.6(7)	
O(1)c–O(1)b	2.73(3)		O(1)c–Zn–O(1)b	80.9(7)	
O(1)b–O(2)	3.25(2)		O(1)b–Zn–O(2)	102.8(7)	
<O–O>	2.95		<O–Zn–O>	90.0	

Table 3. continued

Cd polyhedron				
O(5)a–O(6)g	3.84(3)	x2	O(5)a–Cd–O(6)g	114.2(6)
O(5)a–O(6)h	3.22(3)	x2	O(5)a–Cd–O(6)h	89.5(6)
O(5)a–O(4)	2.71(3)	x2	O(5)a–Cd–O(4)	73.8(6)
O(5)a–O(4)b	3.31(2)	x2	O(5)a–Cd–O(4)b	94.1(6)
O(6)h–O(4)	3.07(2)	x2	O(6)h–Cd–O(4)	82.3(6)
O(6)h–O(6)g	2.62(3)		O(6)h–Cd–O(6)g	67.5(8)
O(4)–O(4)b	4.16(3)		O(4)–Cd–O(4)b	129.0(9)
<O–O>	3.26		<O–Cd–O>	92.0
As(1) tetrahedron				
O(3)–O(5)e	2.85(3)	x2	O(3)–As(1)–O(5)e	113.0(9)
O(3)–O(5)c	2.84(3)	x2	O(3)–As(1)–O(5)c	112.1(8)
O(3)–O(3)d	2.46(3)		O(3)–As(1)–O(3)d	91(1)
O(5)e–O(5)c	2.84(4)		O(5)e–As(1)–O(5)c	113(1)
<O–O>	2.78		<O–As(1)–O>	109.0
As(2) tetrahedron				
O(1)a–O(2)	2.76(2)		O(1)a–As(2)–O(2)	109.0(8)
O(1)a–O(4)b	2.83(3)		O(1)a–As(2)–O(4)b	113.0(8)
O(1)a–O(6)	2.74(2)		O(1)a–As(2)–O(6)	108.5(8)
O(4)b–O(2)	2.70(2)		O(4)b–As(2)–O(2)	105.9(9)
O(4)b–O(6)	2.76(3)		O(4)b–As(2)–O(6)	109.6(8)
O(2)–O(6)	2.77(2)		O(2)–As(2)–O(6)	110.9(8)
<O–O>	2.76		<O–As(2)–O>	109.5

Symmetry operators: a: $\bar{x}+1\frac{1}{2}$, $\bar{y}+\frac{1}{2}$, $\bar{z}+\frac{1}{2}$; b: $\bar{x}+1\frac{1}{2}$, y, $\bar{z}$; c: $x-\frac{1}{2}$, $\bar{y}$, z; d: $\bar{x}+\frac{1}{2}$, y, $\bar{z}$; e: $\bar{x}+1$, $\bar{y}$, $\bar{z}$; f: x, $\bar{y}+\frac{1}{2}$, $z-\frac{1}{2}$; g: $\bar{x}+1$, $\bar{y}+1$, $\bar{z}$; h: $x+\frac{1}{2}$, $\bar{y}+1$, z; i: x, y, $\bar{z}$; j: x, $\bar{y}+\frac{1}{2}$, $z+\frac{1}{2}$

There is one *Cd* site, occupied primarily by Cd, but with some Mn also present. The coordination of the *Cd* site is shown in Figure 2. There are six oxygen atoms in the range 2.21–2.36 Å, and the mean distance of 2.29 Å is in close agreement with the sum of the aggregate radii of the constituent atoms: 2.31 Å. The coordination polyhedron is probably closest to a trigonal prism, but the central cation is almost coplanar with one of the square faces [involving O(4), O(4)b, O(5)a and O(5)f]. As shown in Figure 2, there is quite a short *Cd–W* approach of 2.92 Å through this square face of the coordination polyhedron. However, the bond valence at *Cd* incident from the six nearest anions (Table 4) indicates that the *Cd–W* interaction is not significant.

TABLE 4. BOND VALENCES* (*vu*) FOR KEYITE, CALCULATED FOR BOTH Cu(1) = Cu^{2+} AND Cu(1) = □ (vacancy)

	Cu(2)	Zn	Cd	As(1)	As(2)	Σ	Cu(1) = Cu^{2+}	Σ	Cu(1) = □	H	Σ
O(1)		0.32 0.35			1.20	1.87		1.87			1.87
O(2)		0.41			1.23	1.64	$0.35^{\times2}$↓	1.99	–	$0.24^{\times2}$→	2.12
O(3)	$0.48^{\times2}$↓	0.39		$1.14^{\times2}$↓		2.01		2.01			2.01
O(4)		0.40	$0.33^{\times2}$↓		1.20	1.93		1.93			1.93
O(5)		0.26	$0.44^{\times2}$↓	$1.20^{\times2}$↓		1.90	$0.07^{\times2}$↓	1.97	–		1.90
O(6)	$0.52^{\times2}$↓		$0.29^{\times2}$↓		1.27	2.08		2.08			2.08
W						0.00	$0.58^{\times2}$↓	0.58	–	$0.76^{\times2}$→	2.10
Σ	2.00	2.13	2.12	4.68	4.90		2.00		–	1.00	

* bond-valence curves from Brown & Altermatt (1985)

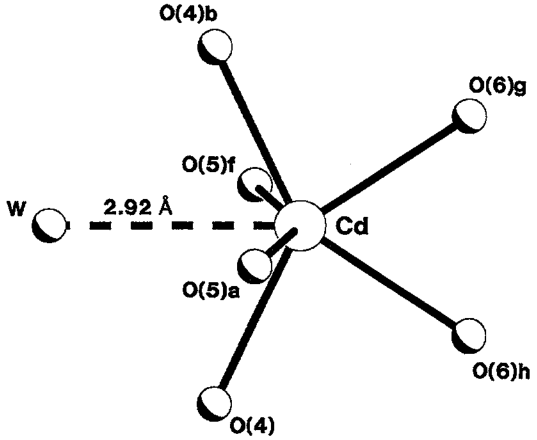

FIG. 2. Coordination around the *Cd* site; note the short *Cd–W* distance.

There are two sites, *As*(1) and *As*(2), both occupied by As^{5+} and surrounded by tetrahedra of oxygen atoms. The observed mean bond-lengths, tetrahedral edge-lengths and angles are typical for tetrahedrally coordinated As^{5+}, although the angular variation of the *As*(1)O_4 tetrahedron is one of the largest recorded for an arsenate structure.

Topology of the structure

Two ZnO_6 octahedra share an edge to form a $[Zn_2O_{10}]$ dimer. These dimers are arranged *en échelon* in the (100) plane and are linked into a sheet by arsenate tetrahedra involving the *As*(2) site (Fig. 3). The arsenate tetrahedra are aligned in rows parallel to [001] at $y \approx 1/8$, 3/8, 5/8 and 7/8; the rows at $y \approx 1/8$ and 3/8 have the tetrahedra pointing in one direction along the *a* axis, and the rows at $y \approx 5/8$ and 7/8 have the tetrahedra pointing in the opposite direction, thus ensuring strong linkage from the *Zn–As*(2) sheet to the adjacent structural elements.

As shown in Figure 1, *Cu*(1)ϕ_6 octahedra share vertices to form a $[M\phi_5]$ corner-sharing chain in which only alternate *Cu*(1) sites are occupied by Cu^{2+}. These chains extend along [001] at $y = 1/4$ and 3/4 [Fig. 4; note that the alternating occupancy of *Cu*(1) by Cu^{2+} and □ is not shown in this figure]. Octahedral vertices are linked by AsO_4 tetrahedra in a staggered arrangement on either side of the chain in the (100) plane (Fig. 4), forming a butlerite-like chain (Moore 1970, Hawthorne 1990, Burns & Hawthorne 1995). However, unlike most of the $[M\phi_5]$-type chains, the remaining octahedral vertices in this plane are linked by atoms occupying the *Cd* site (Fig. 4). Thus we can also consider this motif as an $[M\phi_5]$ chain flanked by two $[MT\phi_8]$ chains (where *M* is a [6]-coordinated cation and *T* is a [4]-coordinated cation) to form a

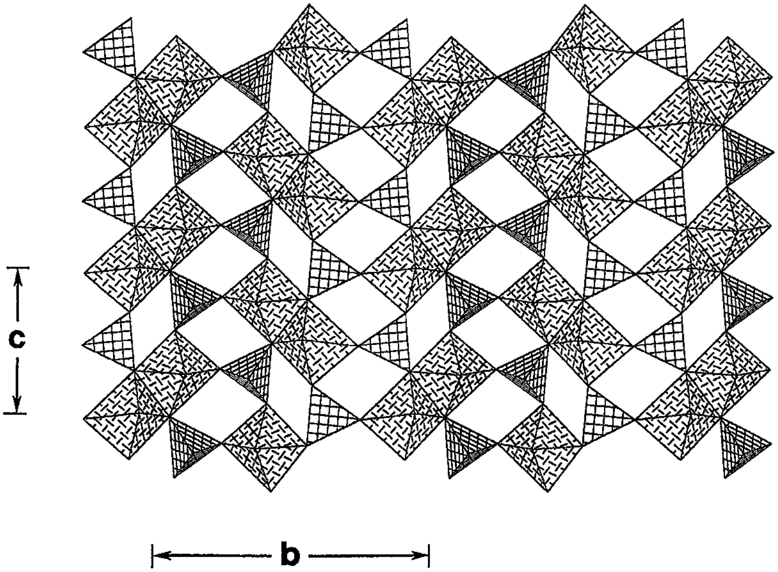

FIG. 3. The *Zn–As*(2) layer at $x = 0.5$ in keyite, projected onto (100); ZnO_6 octahedra are dash-shaded, *As*(2)O_4 tetrahedra are square-lattice-shaded.

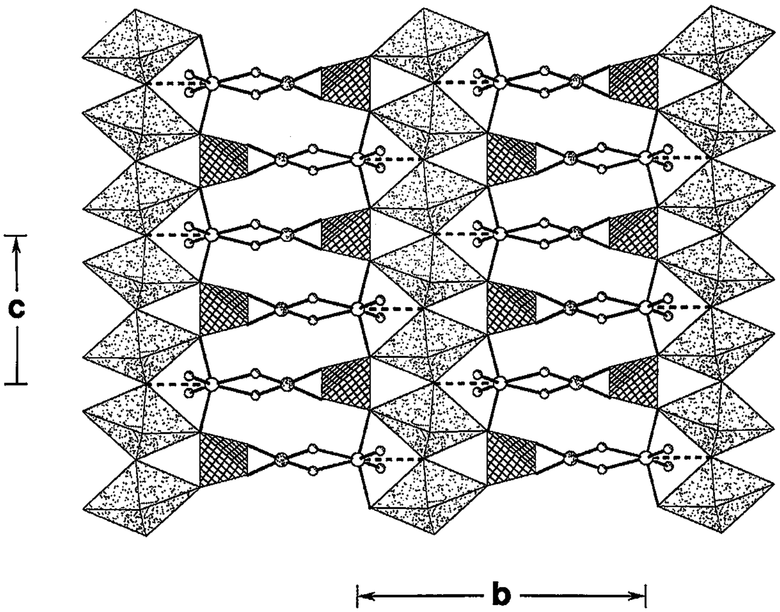

FIG. 4. The *Cu*(1)–*Cu*(2)–*Cd*–*As*(1) layer at $x = 0.25$ in keyite, viewed 12° away from [100]; *Cu*(1)ϕ_6 octahedra are stippled, *As*(1)O_4 tetrahedra are cross-hatched, Cd is shown as a large unshaded circle bonded to six coordinating oxygen atoms (small highlighted circles), and *Cu*(2) is shown as a large highlighted circle in square-planar coordination; the *Cd*–*W* distance of 2.92 Å (Fig. 2) is shown by the broken line.

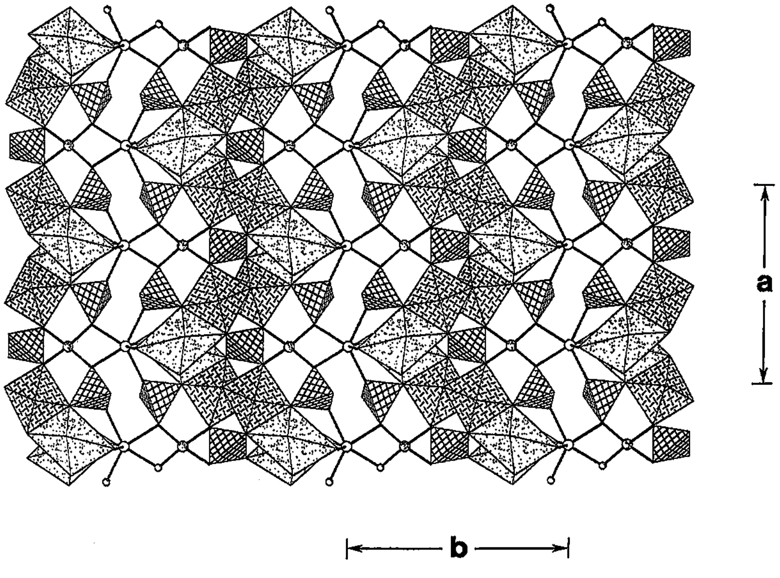

FIG. 5. The structure of keyite projected onto (001); legend as in Figures 3 and 4.

ribbon of the form $[Cu(1)_2Cd_2(AsO_4)_2O_{14}]$, which simplifies to the general form $[M_2(TO_4)\phi_7]$ if vacancies and differences in [6]-coordinated cation species are not considered. These ribbons are cross-linked into a sheet parallel to (100) by Cu^{2+} cations occupying the *Cu*(2) site (Fig. 4). These Cu^{2+} cations occur in square-planar coordination and share edges with $As(1)O_4$ tetrahedra and CdO_6 polyhedra.

The cross-linkage of the sheets of Figures 3 and 4 into a fairly dense framework is shown in Figure 5. ZnO_6 octahedra from one sheet share edges with $Cu(1)O_6$ octahedra of the sandwiching sheets to form an edge-sharing $[Cu(1)_2Zn_2O_{14}W_4]$ tetramer that is further decorated by $As(1)O_4$ and $As(2)O_4$ tetrahedra. Further interlayer linkage is provided by corner-sharing between other coordination polyhedra. We note that our description of the structure as layers parallel to (100) is somewhat arbitrary in terms of bond-valence distribution; we could equally well have chosen layers parallel to any other principal plane, although the description chosen here is perhaps the simplest.

Hydrogen bonding

As shown in Figure 1, each *W* (= H_2O) group is bonded to a single *Cu*(1) cation. Satisfaction of the bond-valence requirements at the oxygen atom of the H_2O group implies that each H atom must be involved in a H-bond of approximately half the bond valence of the *Cu*(1)–*W* bond (Hawthorne 1992, 1994). There are two O(2) anions 2.63 Å from the *W* group, and the local geometry is very well suited to H-bonds between *W* and O(2), as the O(2)–*W*–O(2) angle of 105.6° matches the ideal H–O–H angle of the H_2O group very closely (Fig. 6). This arrangement also fits in with the alternating occupancy and vacancy of the *Cu*(1) site along the [001] direction (*cf.* Figs. 1 and 6). Where the *Cu*(1) site is occupied by Cu^{2+}, the bond-valence incident at the O(2) atom bonded to this Cu^{2+} is close to ideal (Table 4). Where the *Cu*(1) site is vacant, the O(2) anion no longer has a bond-valence contribution from this site. However, the O(2) anion then acts as an acceptor anion for two H-bonds from the adjacent H_2O groups (Fig. 6), and these compensate for the missing *Cu*(1)–O(2) bond (Table 4).

Chemical composition

Solution of the crystal structure has resulted in extensive revision to the chemical formula of keyite. However, the revised formula agrees closely with the original chemical data of Embrey *et al.* (1977). As part of this study, we analyzed keyite by electron microprobe, although not the same crystal that we used to collect the X-ray intensity data (we were unwilling to destroy this crystal after searching so long for an adequately diffracting crystal). The crystal was analyzed on a Cameca SX–50 electron microprobe operating in wavelength-dispersion mode with an excitation voltage of 15 kV, a specimen current of 20 nA, and peak and background counts of 20 and 10 s, respectively. The following standards were used: olivenite (As, Cu), gahnite (Zn), diopside (Ca), spessartine (Mn), Cd metal (Cd), PbTe (Pb). The data were reduced according to the procedures of Pouchou & Pichoir (1984, 1985). All results of analysis are shown in Table 5. One disturbing aspect of the data in Table 5 is the fact that the total wt.% of the oxides exceeds the value of 100.0 by 2.31 wt.%, approximately the amount of H_2O *calculated* from the formula derived from the structure refinement. However, we cannot derive a stereochemically acceptable alternative interpretation of the electron density at the *Cu*(1) and *W* sites.

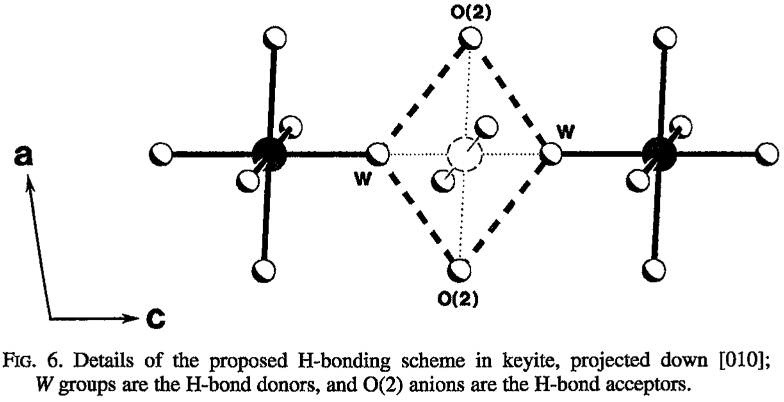

FIG. 6. Details of the proposed H-bonding scheme in keyite, projected down [010]; *W* groups are the H-bond donors, and O(2) anions are the H-bond acceptors.

TABLE 5. CHEMICAL COMPOSITIONS* OF KEYITE FROM THIS STUDY AND FROM EMBREY *et al.* (1977)

	Mean	Min.	Max.	Embrey *et al.* (1977)
As_2O_5 wt%	46.00	45.38	46.78	45.36
ZnO	19.93	17.34	21.74	17.90
CuO	16.61	14.95	19.18	18.81
CdO	14.44	12.20	15.43	14.08
MnO	0.94	0.47	2.60	1.07
CaO	0.53	0.30	0.93	0.80
PbO	1.46	0.18	3.94	0.63
H_2O	(2.40)	-	-	(2.38)
Sum	102.31			101.03
As	6.02			5.98
Zn	3.68			3.33
Cu	3.14			3.58
Cd	1.69			1.66
Mn	0.20			0.23
Ca	0.14			0.21
Pb	0.10			0.05
Sum	14.97			15.04

Cr, V, P, Mg, Si, Fe, S, Ge, Ni, Ti not detected

* Unit formulae calculated on the basis of 26 anions assuming 2 H_2O *pfu*.

Related structures

We can find no mineral or synthetic inorganic structure that shows significant topological similarities to keyite. Embrey *et al.* (1977) suggested that keyite might have a structural relation to stranskiite. This proves not to be the case. Stranskiite, $Zn_2Cu(AsO_4)_2$, has [5]-coordinated Zn (Keller *et al.* 1979), whereas keyite has [6]-coordinated Zn, and the structures are not topologically similar.

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