JENSENITE, A CUPRIC TELLURATE FRAMEWORK STRUCTURE WITH TWO COORDINATIONS OF COPPER

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ABSTRACT

The crystal structure of jensenite, $Cu_3^{2+}Te^{6+}O_6 \cdot 2H_2O$, has been determined and refined to indices $R = 3.3$ and $R_w = 2.5\%$. The structure is monoclinic, $P2_1/n$ (14), with cell parameters a 9.224(2), b 9.180(1), c 7.600(1) Å, β 102.38(1)°, V 628.5(2) Å^3, with $Z = 4$. The structure analysis was essential in determining the valence state of Cu^{2+} and Te^{6+} and the number of O^{2-} atoms and H_2O groups in the formula. The crystal structure of jensenite contains a sheet of fully occupied edge-sharing $[CuO_6]$ and $[TeO_6]$ octahedra. These $(10\bar{1})$ sheets are bonded together through $[Cu_2\varphi_8]$ dimers (where φ represents either O atoms or H_2O groups). The dimers contain two H_2O groups, which reinforce the intersheet linkages *via* H-bonding. The hexagonal closest packed (HCP) layering in jensenite differs from that in other synthetic and natural cupric tellurates in either the sequence of stacking or the composition of the layers.

Keywords: jensenite, crystal structure, tellurate, cupric, dimers.

SOMMAIRE

Nous avons affiné la structure cristalline de la jensenite, $Cu_3^{2+}Te^{6+}O_6 \cdot 2H_2O$, jusqu'à un résidu R de 3.3% ($R_w = 2.5\%$). Il s'agit d'une structure monoclinique, $P2_1/n$ (14), dont les paramètres réticulaires sont a 9.224(2), b 9.180(1), c 7.600(1) Å, β 102.38(1)°, V 628.5(2) Å^3, avec $Z = 4$. L'ébauche de la structure a été essentielle pour établir la valence du cuivre et du tellure (Cu^{2+} et Te^{6+}, respectivement), et la proportion d'atomes O^{2-} et de groupes H_2O dans la formule. La structure contient des feuillets d'octaèdres $[CuO_6]$ et $[TeO_6]$ sans lacunes, partageant leurs arêtes. La liaison d'un tel feuillet $(10\bar{1})$ à un autre est assurée par des dimères $[Cu_2\varphi_8]$ dans lesquels φ représente soit un atome O, soit un groupe H_2O. Les dimères contiennent deux groupes H_2O qui renforcent les liaisons inter-feuillets par des liaisons hydrogène. L'agencement des feuillets à empilement compact hexagonal diffère ici de celui d'autres tellurates cupriques synthétiques ou naturels, soit dans la séquence d'empilement des feuillets, soit dans la composition d'un feuillet.

Mots-clés: jensenite, structure cristalline, tellurate, cuprique, dimères.

INTRODUCTION

Jensenite, described by Roberts *et al.* (1996) from the mineralized dumps of the Centennial Eureka mine, Juab County, Utah, is one of several Cu-bearing tellurates that occur in this deposit. Associated Cu- and Te-bearing minerals include mcalpineite (Roberts *et al.* 1994), xocomecatlite and unnamed $Cu(Mg,Cu,Fe,Zn)_2Te^{6+}O_6 \cdot 6H_2O$. Additional Cu- and Te-bearing secondary minerals that have been found at this locality are cesbronite, frankhawthorneite (Roberts

et al. 1995, Grice & Roberts 1995), dugganite and quetzalcoatlite. Additional information about the geology and mineralogy of the Centennial Eureka mine may be found in Marty *et al.* (1993).

EXPERIMENTAL

The small amount of pure material available precluded standard chemical analytical techniques capable of differentiating the valence states of Cu and Te and establishing the amount of H_2O; the structure-

analysis method (Hawthorne & Grice 1990) has established these quantities; the formula is $Cu_3^{2+}Te^{6+}O_6 \cdot 2H_2O$. Two electron-microprobe analyses (Roberts *et al.* 1996) of the material gave an average of CuO 50.91, ZnO 0.31, TeO_3 38.91, H_2O (from structure analysis) 8.00, total 98.13 wt.%. Based on O = 8, the empirical formula is $(Cu_{2.92}Zn_{0.02})_{\Sigma 2.94}$ $Te^{6+}_{1.01}O_{5.97} \cdot 2.03H_2O$. The ideal formula given above requires CuO 53.00, TeO_3 39.00, H_2O 8.00, total 100 wt.%. It is evident that the material studied is practically ideal, end-member jensenite.

The single crystal of jensenite used for the collection of X-ray-diffraction intensity data (cotype material from the National Mineral Collection of Canada, Systematic Reference Series, catalogue number NMC 67424) is a roughly equant fragment that measures 0.05 × 0.05 × 0.07 mm. Single-crystal precession photographs yielded the unique monoclinic space-group $P2_1/n$ (14), based on systematic absences of reflections. The cell orientation is consistent with $c < a$ (Roberts *et al.* 1996), which leads to the less conventional space-group for this set of systematic absences. Intensity data were collected twice on the same crystal with a fully automated Nicolet $P3$ four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated $MoK\alpha$ radiation. Initially, only one asymmetric unit of intensity data was collected, but the resultant structure-refinement led to poor bond-valence summations. As these summations are critical to the determination of the precise composition of the mineral, a second collection of intensities was necessary, on which the paper is based. This improved data-set lowered the final R values for the refinement, with isotropic thermal parameters, from 7.4 to 5.2%.

A set of 20 reflections was used to orient the crystal and to subsequently refine the cell dimensions. Four asymmetric units of intensity data were collected up to

$2\theta = 60°$ using a $\theta:2\theta$ scan mode (3458 reflections), with scan speeds inversely proportional to intensity, varying from 4 to 29.3°/minute. The merging R for the four asymmetric units is 3.3%. Data pertinent to the collection of intensity data are given in Table 1.

Reduction of the intensity data, structure determination and structure refinement were done with the SHELXTL (Sheldrick 1990) package of computer programs. Data reduction included a correction for background, scaling, Lorentz, polarization and linear absorption. For the ellipsoidal absorption correction, eleven intense diffraction-maxima in the range 17 to 37° 2θ were chosen for ψ diffraction-vector scans after the method of North *et al.* (1968). The merging R for the ψ-scan data set (396 reflections) decreased from 4.4% before the absorption correction to 2.6% after the absorption correction.

CRYSTAL-STRUCTURE ANALYSIS

Assigning phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 1.07, suggesting a centrosymmetric space-group. The structure was

TABLE 1. DATA-COLLECTION INFORMATION FOR JENSENITE

Space Group	$P2_1/n$ (14)	Measured/unique reflections	3458/869
a (Å)	9.224(2)	Observed reflections [>6σ(F)]	605
b (Å)	9.180(1)	Minimum transmission	0.283
c (Å)	7.600(1)	Maximum transmission	0.373
β (°)	102.38(1)	R (%)	3.3
V (Å³)	628.5(2)	R_w (%)	2.5
Unit-cell contents	$4[Cu_3^{2+}Te^{6+}O_6 \cdot 2H_2O]$		
μ (mm^{-1})	14.7	$R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$	$w = [\sigma^2(F_o)]^{-1}$

TABLE 2. POSITIONAL AND THERMAL PARAMETERS (X100, Å²) FOR JENSENITE

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Cu1	0.1209(2)	0.8969(2)	0.1347(2)	1.13(8)	1.91(18)	0.85(5)	-0.16(8)	0.27(5)	0.08(9)	1.29(7)
Cu2	0.1174(3)	0.9229(2)	0.6432(3)	0.77(8)	0.44(18)	1.14(7)	0.00(9)	-0.10(5)	-0.0(1)	0.83(7)
Cu3	0.1200(2)	0.5844(2)	0.6278(2)	0.84(8)	0.45(18)	0.85(6)	0.03(9)	-0.24(5)	-0.1(1)	0.77(7)
Te	-0.1357(1)	0.7564(1)	0.3869(1)	0.83(4)	0.56(10)	0.55(2)	0.00(5)	-0.05(2)	-0.03(6)	0.61(4)
O1	0.241(1)	0.257(1)	0.864(1)	0.3(4)	1.1(9)	0.47(3)	-0.0(4)	-0.3(3)	-0.1(5)	0.6(4)
O2	0.542(1)	0.282(1)	0.868(1)	0.8(5)	1.0(4)	0.7(3)	0.2(4)	-0.0(3)	-0.2(5)	0.9(2)
O3	0.234(1)	0.572(1)	0.881(1)	0.3(5)	0.3(9)	0.5(3)	0.4(4)	-0.0(3)	0.0(4)	0.4(4)
O4	0.503(1)	0.603(1)	0.823(1)	0.9(5)	1.0(4)	1.0(3)	0.3(4)	0.0(3)	-0.1(5)	1.0(2)
O5	0.000(1)	0.596(1)	0.367(1)	0.9(5)	1.9(9)	0.8(3)	0.3(4)	-0.2(3)	0.8(7)	1.3(4)
O6	0.729(1)	0.617(1)	0.443(1)	0.6(4)	1.0(6)	1.2(3)	-0.0(4)	0.0(3)	-0.3(5)	1.0(4)
O7*	0.438(1)	0.655(1)	0.457(1)	1.7(5)	1.2(8)	1.1(3)	0.3(4)	0.0(4)	0.2(4)	1.4(4)
O8*	0.800(1)	0.538(1)	0.806(1)	1.6(5)	2.6(8)	0.9(3)	0.4(4)	0.0(3)	-0.1(5)	1.7(4)

*O7 and O8 are H_2O molecules

Temperature factors are of the form: $\exp[-2\pi^2(U_{11}^2a^{*2} + U_{22}k^2b^{*2} + \ldots 2U_{12}hka^*b^*)]$

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR JENSENITE

Cu1 square pyramid			Cu2 octahedron		
Cu1–O4d	1.973(9)	O4d–O7b 94.6(4)	Cu2–O1c	2.014(10)	O4d–O1c 92.6(3)
Cu1–O6d	1.942(9)	O4d–O7d 88.7(3)	Cu2–O2c	1.947(10)	O4d–O2c 74.4(3)
Cu1–O7b	2.502(10)	O4d–O8c 92.0(4)	Cu2–O3b	1.973(10)	O4d–O3b 97.7(3)
Cu1–O7d	1.978(8)	O6d–O7b 88.3(4)	Cu2–O4b	2.038(11)	O4d–O4b 94.1(3)
Cu1–O8c	1.966(8)	O6d–O7d 88.4(3)	Cu2–O4d	2.444(8)	O4d–O8e 165.3(4)
⟨Cu1–φ⟩eq	1.958	O6d–O8c 91.2(4)	Cu2–O8e	2.319(7)	O1c–O4b 172.2(3)
		O7b–O7d 88.4(4)	⟨Cu2–O⟩eq	(1.992)	O2c–O3b 171.9(3)
		O7b–O8c 90.0(3)	⟨Cu2–O⟩ep	(2.132)	

Cu3 octahedron			Te octahedron		
Cu3–O1c	2.029(10)	O2c–O1c 78.3(4)	Te–O1a	1.941(8)	O1a–O3d 81.6(4)
Cu3–O2c	2.362(10)	O2c–O3 103.7(3)	Te–O2c	1.886(7)	O1a–O4d 91.2(3)
Cu3–O3	1.988(7)	O2c–O5 76.0(3)	Te–O3d	1.975(10)	O1a–O5 94.4(4)
Cu3–O5	2.053(8)	O2c–O5b 106.5(4)	Te–O4d	1.952(10)	O1a–O8a 88.0(4)
Cu3–O5b	2.000(10)	O2c–O6b 168.3(3)	Te–O5	1.953(10)	O1a–O2c 175.3(4)
Cu3–O6b	2.442(10)	O1c–O5b 174.4(3)	Te–O6a	1.898(10)	O3d–O5 173.5(4)
⟨Cu3–O⟩eq	(2.017)	O3–O5 179.4(4)	⟨Te–O⟩	(1.936)	O4d–O6a 178.9(4)
⟨Cu3–O⟩ep	(2.402)				

O–O H-bonded				Cu–Cu distances	
O7–O1c	2.536(12)	O8–O3a	2.671(12)	Cu1–Cu1 3.285(5)	Cu2–Cu2 3.068(4)
O7–O2b	2.580(11)	O8–O5c	2.775(13)	Cu1–Cu2 3.465(3)	Cu2–Cu3 3.047(3)
				Cu1–Cu3 3.834(3)	Cu3–Cu3 3.036(4)

O7 and O8 are H₂O groups

solved and refined in the space group $P2_1/n$. The E-map coordinates were assigned to appropriate scattering curves, and three Cu, one Te and eight O atoms were located. This structure model refined to $R = 5.2\%$.

In the final least-squares refinement, all atomic positions were refined with anisotropic displacement-factors, to final residuals of $R = 3.3\%$ and $R_w = 2.5\%$. The weighting scheme is inversely proportional to $\sigma^2(F)$. The addition of an isotropic extinction-correction did not improve the refinement. Structure refinement in the noncentrosymmetric space-group $P2_1$ did not improve the R values, nor did it indicate in any way that lower symmetry was justified when tested by MISSYM (Le Page 1987). The final positional and thermal parameters are given in Table 2, and selected bond-lengths and angles, in Table 3. A table listing the observed and calculated structure-factors has been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

DESCRIPTION OF THE STRUCTURE

The analysis of the structure of jensenite permitted the calculation of bond-valence sums for the various atomic sites. Based on the constants of Brese & O'Keeffe (1991), the sums are: Cu1 atom 1.96, Cu2 atom 2.02, Cu3 atom 1.90, Te atom 5.70, O1 atom 1.73, O2 atom 1.69, O3 atom 1.74, O4 atom 1.86, O5 atom 1.68, O6 atom 1.86, O7 atom 0.56, and O8 atom 0.46 vu (valence units). These calculations

allow the assignment of the correct valence to the cations Cu^{2+} and Te^{6+} and the recognition of O7 and O8 as H₂O groups. The resultant formula for jensenite is $Cu_3^{2+}Te^{6+}O_6 \cdot 2H_2O$ with $Z = 4$. The low bond-valence sums at the oxygen atom positions is attributed to H-bonding. Each H₂O group is H-bonded to two O atoms at bond distances ranging from 2.54 to 2.78 Å (Table 3). In the structure, there are two $[CuO_6]$ octahedra, one $[TeO_6]$ octahedron and a $[CuO_2(H_2O)_3]$ (subsequently designated $[Cu\varphi_5]$) square pyramid. The $[Cu\varphi_5]$ square pyramids link to form isolated edge-sharing $[Cu_2\varphi_8]$ dimers (Fig. 1). These dimers are the most common polyhedron for 5-fold coordinated Cu in mineral structures, and several examples are given by Eby & Hawthorne (1993). Mineral structures that contain these dimers are blossite, kinoite, libethenite, olivenite, stoiberite, stranskiite, and ziesite. From Table 3, it can be seen that the $[Cu\varphi_n]$ polyhedra are distorted from regular octahedral and regular square-pyramidal coordination. The Jahn–Teller effect on the Cu^{2+} cation is evident in each octahedron; its elongate axes have bond lengths (Cu2–O4: 2.44 Å, Cu2–O5: 2.32 Å, Cu3–O2: 2.36 Å and Cu3–O6: 2.44 Å) which are much longer in comparison to the average (1.992 Å and 2.017 Å) for the other four Cu2–O and Cu3–O bonds. The elongate square pyramid's axis has a Cu1–O bond length of 2.502 Å, whereas the average for the other four is 1.956 Å (predictably shorter than those bonds in the square-equatorial plane of the
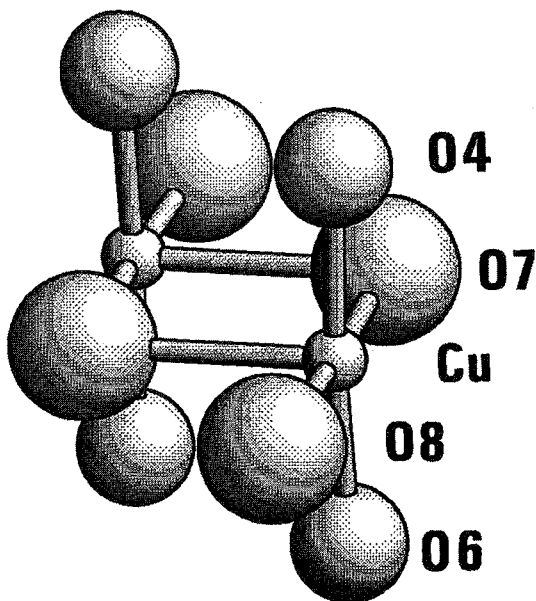

FIG. 1. The $[Cu_2O_2(H_2O)]$ dimers in jensenite. The water groups (represented by the largest spheres) are denoted as O7 and O8.
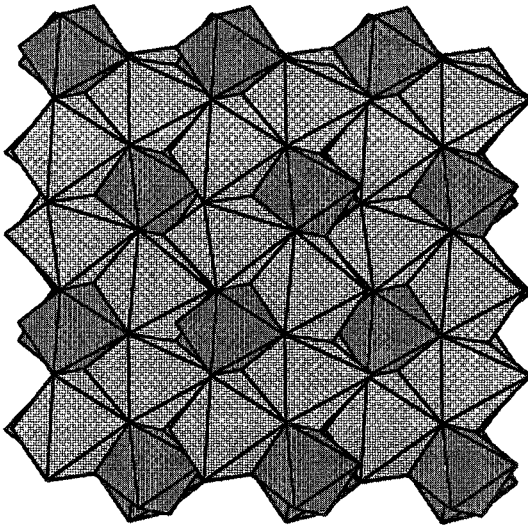
FIG. 2. The {10$\bar{1}$} HCP layer in the jensenite structure. The [CuO$_6$] octahedra are shown with light shading, and the [TeO$_6$] octahedra, with dark shading.

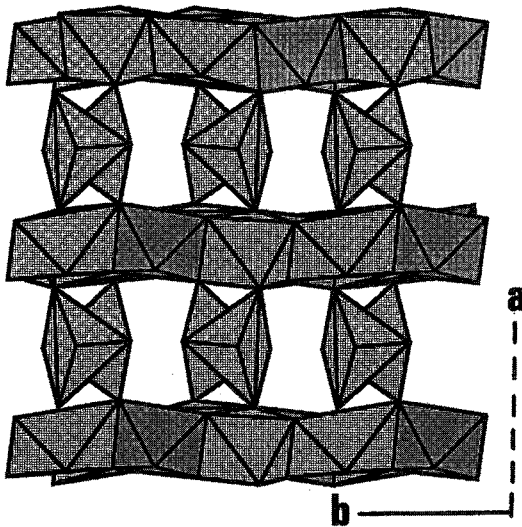octahedra). The Cu–Cu distance within the [Cu$_2\varphi_8$] dimer (3.28 Å) is not significantly different from Cu–Cu distances between adjacent Cu octahedra (Table 3). The [TeO$_6$] octahedron is regular, with an average Te–O bond length of 1.936 Å (Table 3).

The crystal structure of jensenite contains a sheet of fully occupied edge-sharing [CuO$_6$] and [TeO$_6$] octahedra; the sheet composition is [Cu$_2$TeO$_6$] (Fig. 2). The sheets are parallel to the cleavage plane (10$\bar{1}$), and adjacent sheets are bonded together through [Cu$_2\varphi_8$] dimers (Fig. 3). The [Cu$_2\varphi_8$] dimers contain two H$_2$O groups, which reinforce the intersheet bonding via H-bonding.

Eby & Hawthorne (1993) classified this type of copper oxysalt structure as an infinite framework $M = M – M = M$, where the M denotes cations in octahedral or square-pyramidal coordination, the double hyphen denotes edge sharing, and the single hyphen denotes corner sharing.

To date, there are two other cupric tellurate minerals that have been structurally characterized: frank-hawthorneite, Cu$_2$TeO$_4$(OH)$_2$ (Grice & Roberts 1995) and parakhinite, Cu$_3$PbTeO$_6$(OH)$_2$ (Burns et al. 1995). Like jensenite, both structures consist of hexagonal closest packed (HCP) layers, but of differing kinds. In jensenite, there is a fully occupied single HCP layer. In frankhawthorneite, the HCP layers have one-half of the octahedrally coordinated sites occupied. Each layer has the unique ribbon with a [Teφ_6] octahedron alternating with a [Cuφ_6] doublet of octahedra (Grice & Roberts 1995). The stacking sequence of these layers is ...ABAB... . In parakhinite, the HCP layers are also one-half occupied and have a stacking sequence ....ABAB...., but the individual layers have differing compositions and contain edge-sharing chains similar to those found in rutile (see Fig. 3a, Grice & Roberts 1995). These double layers are cross-linked by [Pbφ_8] polyhedra and H-bonding. The structure of synthetic Cu$_3$TeO$_6$ (Falck et al. 1978) has fully occupied HCP layers with a stacking sequence ...AAAA... along [111]. These layers are linked by corner-sharing octahedra. It is of interest to note that the hydrated equivalent of this synthetic phase, jensenite, adopts a different composition of the HCP layer and, in addition, one of the Cu atoms is in square-pyramidal coordination.

a

b

FIG. 3. The [101]-axis projection of the jensenite structure showing the HCP layer with [CuO$_6$] octahedra (light shading), [TeO$_6$] octahedra (dark shading) and the interlayer [Cu$_2\varphi_8$] dimers (also light shading). The H$_2$O groups, as part of the dimers, lie in a plane midway between the layers of octahedra.

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