



analysis method (Hawthorne & Grice 1990) has established these quantities; the formula is  $\text{Cu}_3^{2+}\text{Te}^{6+}\text{O}_6 \cdot 2\text{H}_2\text{O}$ . Two electron-microprobe analyses (Roberts *et al.* 1996) of the material gave an average of CuO 50.91, ZnO 0.31,  $\text{TeO}_3$  38.91,  $\text{H}_2\text{O}$  (from structure analysis) 8.00, total 98.13 wt.%. Based on  $\text{O} = 8$ , the empirical formula is  $(\text{Cu}_{2.92}\text{Zn}_{0.02})_{\Sigma 2.94}\text{Te}^{6+}_{1.01}\text{O}_{5.97} \cdot 2.03\text{H}_2\text{O}$ . The ideal formula given above requires CuO 53.00,  $\text{TeO}_3$  39.00,  $\text{H}_2\text{O}$  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  $0.05 \times 0.05 \times 0.07$  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  $\text{MoK}\alpha$  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

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 $>6\sigma(F)$	605
$b$ (Å)	9.180(1)	Minimum transmission	0.283
$c$ (Å)	7.800(1)	Maximum transmission	0.373
$\beta$ (°)	102.38(1)	$R$ (%)	3.3
$V$ (Å <sup>3</sup> )	628.5(2)	$R_w$ (%)	2.5
Unit-cell contents	$4[\text{Cu}_{2.92}\text{Te}^{6+}\text{O}_{5.97} \cdot 2\text{H}_2\text{O}]$		
$\mu$ (mm <sup>-1</sup> )	14.7	$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$	$w = [\sigma^2(F_o)]^{-1}$

$2\theta = 60^\circ$  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  $37^\circ 2\theta$  were chosen for  $\psi$  diffraction-vector scans after the method of North *et al.* (1968). The merging  $R$  for the  $\psi$ -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 2. POSITIONAL AND THERMAL PARAMETERS ( $\times 100, \text{Å}^2$ ) FOR JENSENITE

Site	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
Cu1	0.1208(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)	0.8432(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(8)	0.03(9)	-0.24(5)	-0.1(1)	0.77(7)
Te	-0.1357(1)	0.7594(1)	0.3869(1)	0.83(4)	0.58(10)	0.55(2)	0.00(5)	-0.05(2)	-0.03(6)	0.61(4)
O1	0.241(1)	0.257(1)	0.884(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)	0.397(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(9)	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)	0.808(1)	1.8(5)	2.6(3)	0.9(3)	0.4(4)	0.0(3)	-0.1(5)	1.7(4)

\*O7 and O8 are  $\text{H}_2\text{O}$  molecules

Temperature factors are of the form:  $\exp[-2\alpha^2(U_{11}a^2 + U_{22}b^2 + \dots + 2U_{12}hka'b)]$

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	1.873(10)	O4d-O3b	97.7(3)
Cu1-O7d	1.978(8)	O9d-O7b	88.3(4)	Cu2-O4b	2.038(11)	O4d-O4b	94.1(3)
Cu1-O8c	1.969(8)	O9d-O7d	88.4(3)	Cu2-O4d	2.444(9)	O4d-O8e	195.3(4)
(Cu1- $\varphi$ ) <sub>sq</sub>	1.958	O9d-O8c	91.2(4)	Cu2-O8e	2.319(7)	O1c-O4b	172.2(3)
		O7b-O7d	86.4(4)	(Cu2-O) <sub>oct</sub>	(1.992)	O2c-O3b	171.9(3)
		O7b-O8c	90.0(3)	(Cu2-O) <sub>sp</sub>	(2.132)		
Cu3 octahedron			Te octahedron				
Cu3-O1c	2.029(10)	O2c-O1c	78.3(4)	Te-O1a	1.941(9)	O1a-O3d	81.6(4)
Cu3-O2c	2.362(10)	O2c-O3	103.7(3)	Te-O2c	1.898(7)	O1a-O4d	91.2(3)
Cu3-O3	1.888(7)	O2c-O5	76.0(3)	Te-O3d	1.975(10)	O1a-O5	94.4(4)
Cu3-O5	2.053(9)	O2c-O5b	106.5(4)	Te-O4d	1.952(10)	O1a-O6a	88.0(4)
Cu3-O5b	2.000(10)	O2c-O6b	168.3(3)	Te-O5	1.953(10)	O1a-O2c	175.3(4)
Cu3-O8b	2.442(10)	O1c-O5b	174.4(4)	Te-O8a	1.898(10)	O3d-O5	173.5(4)
(Cu3-O) <sub>oct</sub>	(2.017)	O3-O5	179.4(4)	(Te-O)	(1.936)	O4d-O6a	178.9(4)
(Cu3-O) <sub>sp</sub>	(2.402)						
O-O H-bonded			Cu-Cu distances				
O7-O1c	2.538(12)	O8-O3a	2.671(12)	Cu1-Cu1	3.285(5)	Cu2-Cu2	3.088(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	3.038(4)

O7 and O8 are H<sub>2</sub>O 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<sup>2+</sup> and Te<sup>6+</sup> and the recognition of O7 and O8 as H<sub>2</sub>O groups. The resultant formula for jensenite is Cu<sub>3</sub><sup>2+</sup>Te<sup>6+</sup>O<sub>6</sub>·2H<sub>2</sub>O with  $Z = 4$ . The low bond-valence sums at the oxygen atom positions is attributed to H-bonding. Each H<sub>2</sub>O 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<sub>6</sub>] octahedra, one [TeO<sub>6</sub>] octahedron and a [CuO<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>] (subsequently designated [Cu $\varphi$ <sub>5</sub>] square pyramid. The [Cu $\varphi$ <sub>5</sub>] square pyramids link to form isolated edge-sharing [Cu $\varphi$ <sub>8</sub>] 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 $\varphi$ <sub>n</sub>] polyhedra are distorted from regular octahedral and regular square-pyramidal coordination. The Jahn-Teller effect on the Cu<sup>2+</sup> 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

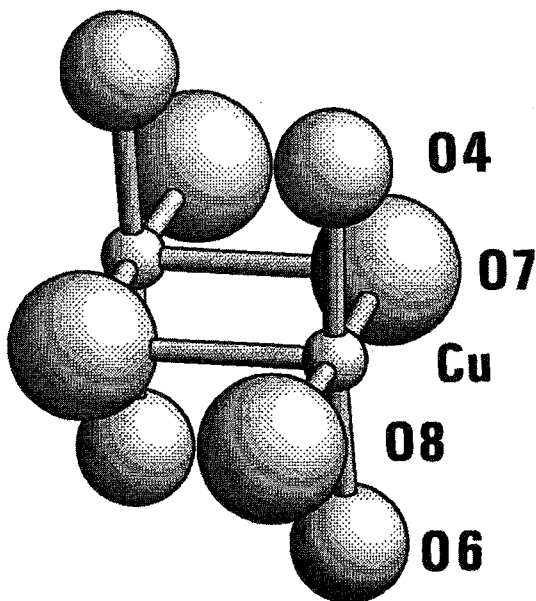


FIG. 1. The [Cu<sub>2</sub>O<sub>2</sub>(H<sub>2</sub>O)] dimers in jensenite. The water groups (represented by the largest spheres) are denoted as O7 and O8.

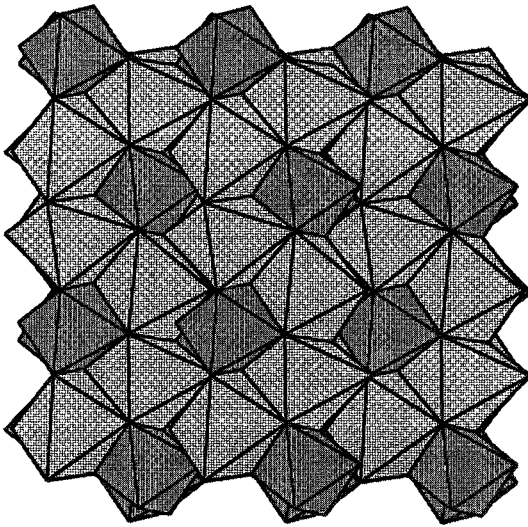


FIG. 2. The  $\{10\bar{1}\}$  HCP layer in the jensenite structure. The  $[\text{CuO}_6]$  octahedra are shown with light shading, and the  $[\text{TeO}_6]$  octahedra, with dark shading.

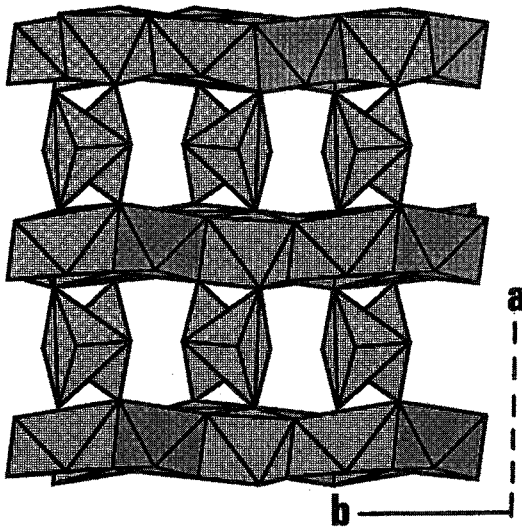


FIG. 3. The  $[101]$ -axis projection of the jensenite structure showing the HCP layer with  $[\text{CuO}_6]$  octahedra (light shading),  $[\text{TeO}_6]$  octahedra (dark shading) and the interlayer  $[\text{Cu}_2\text{O}_8]$  dimers (also light shading). The  $\text{H}_2\text{O}$  groups, as part of the dimers, lie in a plane midway between the layers of octahedra.

octahedra). The Cu–Cu distance within the  $[\text{Cu}_2\text{O}_8]$  dimer (3.28 Å) is not significantly different from Cu–Cu distances between adjacent Cu octahedra (Table 3). The  $[\text{TeO}_6]$  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  $[\text{CuO}_6]$  and  $[\text{TeO}_6]$  octahedra; the sheet composition is  $[\text{Cu}_2\text{TeO}_6]$  (Fig. 2). The sheets are parallel to the cleavage plane  $(10\bar{1})$ , and adjacent sheets are bonded together through  $[\text{Cu}_2\text{O}_8]$  dimers (Fig. 3). The  $[\text{Cu}_2\text{O}_8]$  dimers contain two  $\text{H}_2\text{O}$  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: frankhawthorneite,  $\text{Cu}_2\text{TeO}_4(\text{OH})_2$  (Grice & Roberts 1995) and parakhinite,  $\text{Cu}_3\text{PbTeO}_6(\text{OH})_2$  (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  $[\text{TeO}_6]$  octahedron alternating with a  $[\text{CuO}_6]$  doublet of octahedra (Grice & Roberts 1995). The stacking sequence of these layers is  $\dots\text{ABAB}\dots$ . In parakhinite, the HCP layers are also one-half occupied and have a stacking sequence  $\dots\text{ABAB}\dots$ , 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  $[\text{PbO}_6]$  polyhedra and H-bonding. The structure of synthetic  $\text{Cu}_3\text{TeO}_6$  (Falck *et al.* 1978) has fully occupied HCP layers with a stacking sequence  $\dots\text{AAAA}\dots$  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.

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## REFERENCES

- BRESE, N.E. & O'KEEFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.
- BURNS, P.C., COOPER, M.A. & HAWTHORNE, F.C. (1995): Parakhinite,  $\text{Cu}_3^{2+}\text{PbTe}^{6+}\text{O}_6(\text{OH})_2$ : crystal structure and revision of chemical formula. *Can. Mineral.* **33**, 33-40.
- EBY, R.K. & HAWTHORNE, F.C. (1993): Structural relations in copper oxysalt minerals. I. Structural hierarchy. *Acta Crystallogr.* **B49**, 28-56.
- FALCK, L., LINDQVIST, O. & MORET, J. (1978): Tricopper(II) tellurate(VI). *Acta Crystallogr.* **B34**, 896-897.
- GRICE, J.D. & ROBERTS, A.C. (1995): Frankhawthorneite, a unique HCP framework structure of cupric tellurate. *Can. Mineral.* **33**, 649-653.
- HAWTHORNE, F.C. & GRICE, J.D. (1990): Crystal-structure analysis as a chemical analytical method: application to light elements. *Can. Mineral.* **28**, 693-702.
- LE PAGE, Y. (1987): Computer derivation of the symmetry elements implied in a structure description. *J. Appl. Crystallogr.* **20**, 264-269.
- MARTY, J., JENSEN, M.C. & ROBERTS, A.C. (1993): Minerals of the Centennial Eureka mine, Tintic district, Eureka, Utah. *Rocks and Minerals* **68**, 406-416.
- NORTH, A.C.T., PHILLIPS, D.C. & MATHEWS, F.S. (1968): A semi-empirical method of absorption correction. *Acta Crystallogr.* **A24**, 351-359.
- ROBERTS, A.C., ERCIT, T.S., CRIDDLE, A.J., JONES, G.C., WILLIAMS, R.S., CURETON, F.E., II & JENSEN, M.C. (1994): Mcalpineite,  $\text{Cu}_3\text{TeO}_6\text{H}_2\text{O}$ , a new mineral from the McAlpine mine, Tuolumne County, California and from the Centennial Eureka mine, Juab County, Utah. *Mineral. Mag.* **58**, 417-424.
- , GRICE, J.D., CRIDDLE, A.J., JENSEN, M.C., HARRIS, D.C. & MOFFATT, E.A. (1995): Frankhawthorneite,  $\text{Cu}_2\text{Te}^{6+}\text{O}_4(\text{OH})_2$ , a new mineral species from the Centennial Eureka mine, Tintic District, Juab County, Utah. *Can. Mineral.* **33**, 641-647.
- , —————, GROAT, L.A., CRIDDLE, A.J., GAULT, R.A., ERD, R.C. & MOFFATT, E.A. (1996): Jensenite,  $\text{Cu}_3\text{Te}^{6+}\text{O}_6\cdot 2\text{H}_2\text{O}$ , a new mineral species from the Centennial Eureka mine, Tintic District, Juab County, Utah. *Can. Mineral.* **34**, 49-54.
- SHELDRIK, G.M. (1990): *SHELXTL, a Crystallographic Computing Package* (revision 4.1). Siemens Analytical Instruments, Inc., Madison, Wisconsin.

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