

Fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, a new vanadium sublimate from Izalco volcano, El Salvador: crystal structure

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Abstract

Fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, is triclinic with $a = 8.1576(6)$, $b = 8.2691(5)$, $c = 8.0437(7)\text{\AA}$, $\alpha = 107.144(5)^\circ$, $\beta = 91.389(7)^\circ$, $\gamma = 106.441(5)^\circ$, $Z = 1$, and space group $P\bar{1}$. The crystal structure has been solved and refined to a weighted R of 0.044 from 2875 intensities measured on a four-circle diffractometer. The structure consists of vanadium in tetrahedral coordination and copper in octahedral and trigonal bipyramidal coordination with Jahn-Teller distortions typical for Cu^{2+} . The octahedra form a sheet with holes and are cross-linked by vanadium tetrahedra and copper trigonal bipyramids.

Introduction

Fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, a fumarolic mineral from Izalco volcano, El Salvador, is described in the preceding paper (Hughes and Hadidiacos, 1985). It is a double honor to have the mineral named after me and to have the opportunity to solve and present its crystal structure.

Experimental

A crystal of fingerite, $0.09 \times 0.09 \times 0.15$ mm, was mounted on a four-circle diffractometer, and the orientation matrix and reduced unit cell were determined by an automatic indexing algorithm similar to that suggested by Jacobson (1976). The cell proposed by Hughes and Hadidiacos (1985) was confirmed. In the final orientation the axis of crystal rotation was approximately parallel to $[3\bar{8}2]$. Unit-cell and orientation parameters were refined from the positions of 20 independent observations with $39^\circ \leq 2\theta \leq 54^\circ$ measured by the eight-reflection centering method of King and Finger (1979). The unit cell and other crystal data are listed in Table 1.

The intensity data for one hemisphere ($l \geq 0$) of the triclinic mineral were measured to $60^\circ 2\theta$ with omega step scans and Nb-filtered Mo radiation. The resulting data were integrated by application of the Lehmann and Larsen (1974) technique for optimum background selection. In accordance with the suggestions of Gabe (1980), the inner edge of the background region was selected two steps outside the point corresponding to the minimum in σ/I . Integrated intensities were corrected for Lorentz-polarization and absorption effects ($\mu_1 = 143.2 \text{ cm}^{-1}$) with the program of Burnham (1966). A total of 2875 intensities were measured. Of these, 2257 had values greater than twice the standard deviation.

Solution of the crystal structure was accomplished through use of the tangent formula as implemented in MULTAN-80 and associated programs (Main et al., 1980). Pseudosymmetry of the copper and vanadium atoms resulted in some difficulty in the solution (cf. Hai-Fu et al., 1983). In addition, the formula as derived from electron microprobe analyses was thought to be $\text{Cu}_{10}\text{V}_6\text{O}_{25}$. Despite these difficulties, successive cycles of

Fourier syntheses revealed the positions of all atoms, the correct stoichiometry and confirmation of the space group ($P\bar{1}$).

Program RFINE4 (Finger and Prince, 1975) was used to refine the structure. Effective standard deviations, σ' , used to calculate least-squares weights, were calculated from the formula $\sigma'^2 = \sigma^2 + (0.012F)^2$, where σ is the standard deviation derived from counting statistics and F is the structure factor. All structure-factor calculations were performed with neutral atom scattering curves selected from the data of Cromer and Mann (1968). Anomalous dispersion coefficients were taken from *International Tables for X-Ray Crystallography, Vol. IV* (1974). The refined structure converged to an R factor of 7.6% with isotropic temperature factors and an isotropic secondary extinction coefficient. After conversion to anisotropic temperature factors, the structure converged to a weighted R of 4.4% and an unweighted R of 4.6%. The anisotropic refinement is significantly better than the isotropic calculation (Hamilton, 1965). Robust/resistant techniques (Prince, 1982) were employed in the final stages of the refinement. Final observed and calculated structure factors are listed in Table 2.¹ Refined atomic coordinates and equivalent isotropic temperature factors are listed in Table 3.

Description of the structure

The anion arrangement of $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$ may be described as essentially a close-packed array of oxygen. Octahedrally coordinated copper ions form a sheet with holes (Fig. 1). These edge-shared polyhedra have Jahn-Teller distortion typical for Cu^{2+} (Shannon and Calvo, 1973). Each octahedron has four equatorial oxygen ions at distances approximately equal to 2\AA (Table 4) and two apical oxygens at greater distances. For Cu3 and Cu4, the

¹ To receive a copy of Table 2, order Document AM-85-258 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D. C. 20009. Please remit \$5.00 in advance for the microfiche.

Table 1. Crystal data for fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, at 28°C.

Parameter	Value
a , Å	8.1576(6)*
b	8.2691(5)
c	8.0437(7)
α , °	107.144(5)
β	91.389(7)
γ	106.441(5)
V , Å ³	493.84(6)
Space group	$P1$
Z	1
X-ray density, $\text{g}\cdot\text{cm}^{-3}$	4.776

*Number in parentheses represents one standard deviation.

longest distance is greater than 2.9Å. Calculated bond valences for these distances (Brown, 1981) are 0.04 valence unit; thus these ions could also be considered to be 5-coordinated. If that were the case, the cation would lie very near the surface of the polyhedron as it is in the

Table 3. Atom coordinates and equivalent isotropic temperature factors for fingerite

Atom	x	y	z	B_{eq} , Å ²
Cu1	0	0	0	0.56(2)*
Cu2	0.8410(1)	0.1455(1)	0.7221(1)	0.64(2)
Cu3	0.7046(1)	0.3372(1)	0.5008(1)	0.57(2)
Cu4	0.5807(1)	0.5078(1)	0.2771(1)	0.71(2)
Cu5	0.7845(1)	0.2522(1)	0.1266(1)	0.60(2)
Cu6	0.3711(1)	0.1460(1)	0.1485(1)	1.12(2)
V1	0.9025(2)	0.7537(2)	0.5675(2)	0.41(2)
V2	0.1871(2)	0.4376(2)	0.0781(2)	0.38(2)
V3	0.5887(2)	0.9348(2)	0.2667(2)	0.39(2)
O1	0.7055(7)	0.5757(7)	0.5131(6)	0.64(8)
O2	0.7876(7)	0.4785(7)	0.0891(7)	0.70(8)
O3	0.3628(7)	0.3700(7)	0.1138(7)	0.74(8)
O4	0.8183(7)	0.3911(7)	0.7404(7)	0.68(8)
O5	-0.0003(7)	0.2491(7)	0.0200(7)	0.57(8)
O6	0.9502(7)	0.3256(7)	0.3768(7)	0.82(8)
O7	0.3804(7)	0.9268(7)	0.1814(7)	0.61(8)
O8	0.7287(7)	-0.0093(7)	0.1150(7)	0.65(8)
O9	0.1243(7)	0.0730(7)	0.2405(7)	0.61(8)
O10	0.4024(7)	0.7224(7)	0.7369(7)	0.53(8)
O11	0.3323(7)	0.9133(7)	0.5331(7)	0.72(8)
O12	0.4286(7)	0.2645(7)	0.7179(7)	1.05(9)
O13	0.9546(7)	0.8185(7)	0.3937(7)	0.78(8)

*Number in parentheses represents one standard deviation.

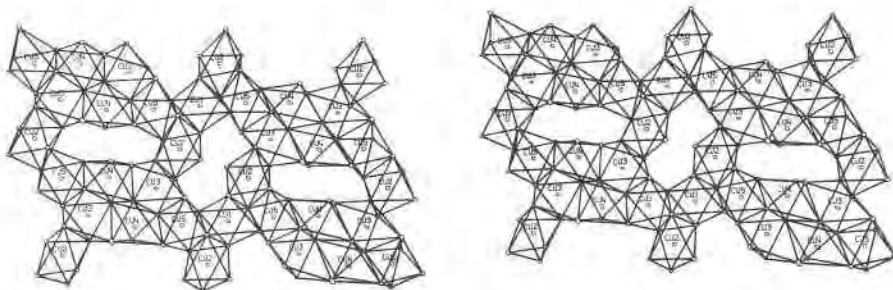


Fig. 1. A stereo projection of a portion of the structure of fingerite showing the sheets of $\text{Cu}-\text{O}_6$ octahedra with holes. The structure is viewed approximately parallel to $[382]$. The origin coincides with Cu1, and small circles represent other inversion centers.

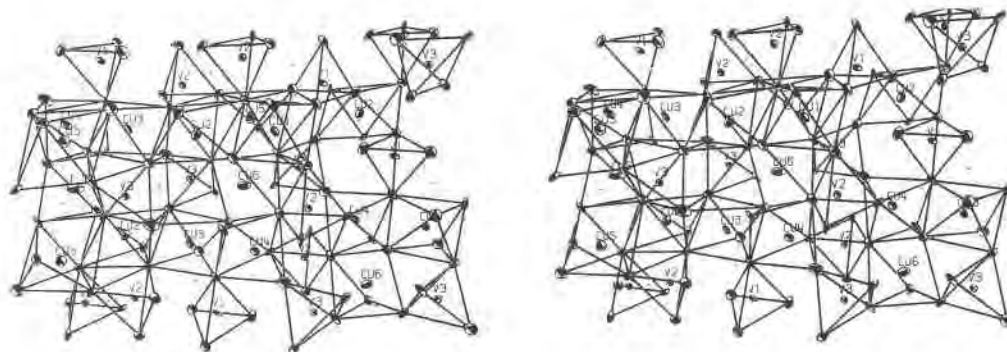


Fig. 2. Stereo projection representing details of the $\text{V}-\text{O}_4$ tetrahedra and the $\text{Cu}-\text{O}_5$ trigonal bipyramid cross-linking the sheets of octahedra in fingerite. The projection direction is approximately parallel to $[211]$.

Table 4. Bond distances and angles in fingerite

Cu1-05 (2x)	2.019 (5)* \AA	05-Cu1-09	86.5 (2) $^\circ$	05-Cu1-08	98.7 (2)
-09 (2x)	2.001 (5)	05-Cu1-09	93.5 (2)	09-Cu1-08	88.3 (2)
-08 (2x)	2.409 (5)	05-Cu1-08	81.3 (2)	09-Cu1-08	91.6 (2)
Mean	2.143				
Cu2-04	2.054 (4)	04-Cu2-07	92.6 (2)	07-Cu2-011	84.4 (2)
-07	1.988 (5)	04-Cu2-09	167.8 (2)	09-Cu2-013	90.7 (2)
-09	2.011 (5)	04-Cu2-013	93.6 (2)	09-Cu2-05	74.8 (2)
-013	1.922 (5)	04-Cu2-05	93.5 (2)	09-Cu2-011	113.5 (2)
-05	2.482 (5)	04-Cu2-011	77.8 (2)	013-Cu2-05	94.5 (2)
-011	2.309 (5)	07-Cu2-09	84.2 (2)	013-Cu2-011	91.8 (2)
Mean	2.128	07-Cu2-013	171.8 (2)	05-Cu2-011	169.5 (2)
		07-Cu2-05	90.3 (2)		
Cu3-01	1.944 (5)	01-Cu3-04	98.6 (2)	04-Cu3-012	73.7 (2)
-04	1.987 (5)	01-Cu3-010	83.2 (2)	010-Cu3-011	89.6 (2)
-010	1.944 (5)	01-Cu3-011	170.8 (2)	010-Cu3-06	85.7 (2)
-011	1.941 (5)	01-Cu3-06	100.6 (2)	010-Cu3-012	107.4 (2)
-06	2.273 (6)	01-Cu3-012	97.7 (2)	011-Cu3-06	84.5 (2)
-012	2.919 (6)	04-Cu3-010	177.8 (2)	011-Cu3-012	78.9 (2)
Mean	2.168	04-Cu3-011	88.7 (2)	06-Cu3-012	158.7 (2)
		04-Cu3-06	92.8 (2)		
Cu4-01	1.977 (5)	01-Cu4-03	147.8 (2)	03-Cu4-02	101.5 (2)
-03	2.010 (5)	01-Cu4-010	83.0 (2)	010-Cu4-012	177.1 (2)
-010	1.918 (5)	01-Cu4-012	98.2 (2)	010-Cu4-01a	85.1 (2)
-012	1.895 (6)	01-Cu4-01a	78.3 (2)	010-Cu4-02	77.8 (2)
-01a	2.956 (6)	01-Cu4-02	104.5 (2)	012-Cu4-01a	97.7 (2)
-02	2.309 (6)	03-Cu4-010	84.3 (2)	012-Cu4-02	99.4 (2)
Mean	2.178	03-Cu4-012	96.0 (2)	01a-Cu4-02	162.1 (2)
		03-Cu4-01a	71.2 (2)		
Cu5-02	1.975 (5)	02-Cu5-05	92.8 (2)	05-Cu5-07	87.6 (2)
-05	1.976 (5)	02-Cu5-08	165.1 (2)	08-Cu5-010	90.8 (2)
-08	2.053 (6)	02-Cu5-010	86.5 (2)	08-Cu5-06	88.6 (2)
-010	1.923 (5)	02-Cu5-06	105.9 (2)	08-Cu5-07	74.9 (2)
-06	2.220 (5)	02-Cu5-07	91.2 (2)	010-Cu5-06	87.7 (2)
-07	2.586 (5)	05-Cu5-08	92.0 (2)	010-Cu5-07	101.2 (2)
Mean	2.122	05-Cu5-010	171.2 (2)	06-Cu5-07	161.3 (2)
		05-Cu5-06	84.1 (2)		
Cu6-03	1.971 (5)	03-Cu6-07	179.6 (2)	07-Cu6-09	82.1 (2)
-07	1.929 (5)	03-Cu6-08	89.8 (2)	07-Cu6-010	94.2 (2)
-08	2.102 (5)	03-Cu6-09	98.3 (2)	08-Cu6-09	93.2 (2)
-09	2.147 (6)	03-Cu6-010	85.7 (2)	08-Cu6-010	133.2 (2)
-010	1.907 (5)	07-Cu6-08	90.0 (2)	09-Cu6-010	133.5 (2)
Mean	2.011				
V1-01	1.785 (6)	01-V1-06	106.3 (3)	06-V1-09	108.9 (2)
-06	1.634 (6)	01-V1-09	107.0 (2)	06-V1-013	108.8 (3)
-09	1.837 (5)	01-V1-013	110.2 (3)	09-V1-013	115.2 (3)
-013	1.662 (5)				
Mean	1.730				
V2-02	1.678 (5)	02-V2-03	109.4 (3)	03-V2-04	108.6 (3)
-03	1.725 (5)	02-V2-04	106.3 (3)	03-V2-05	108.6 (2)
-04	1.720 (5)	02-V2-05	108.5 (3)	04-V2-05	115.3 (2)
-05	1.781 (5)				
Mean	1.726				
V3-07	1.793 (5)	07-V3-08	105.7 (2)	08-V3-011	108.1 (3)
-08	1.763 (6)	07-V3-011	115.3 (2)	08-V3-012	113.0 (3)
-011	1.699 (5)	07-V3-012	106.8 (3)	011-V3-012	108.0 (3)
-012	1.655 (6)				
Mean	1.728				

*Number in parentheses represents one standard deviation.

plane of the four equatorial oxygens. The octahedral sheets are cross-linked by V-O₄ tetrahedra and a Cu-O₅ trigonal bipyramid (Fig. 2). The latter polyhedron is more regular than the bipyramids found by Shannon and Calvo (1973); however, the mean Cu-O is similar.

A complete set of valence sums for all ions has been computed by the method of Brown (1981). The range of values for Cu is from 1.83 to 2.10, for V from 4.86 to 4.96, and for O from 1.86 to 2.09. These values are compatible with the anticipated formal valences of these ions.

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