

The Crystal Structure of Getchellite, AsSbS₃

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Getchellite, AsSbS₃, is monoclinic, space group $P2_1/a$, with $a=11.8568$ (7), $b=9.0152$ (4), $c=10.1938$ (5) Å, and $\beta=116.365$ (4)°. $D_m=3.92$ (3) and $D_x=3.98$ g cm⁻³ for $Z=8$ AsSbS₃ per cell. Diffraction data were recorded from a synthetic crystal using an equi-inclination diffractometer equipped with a proportional counter as detector. Crystals of getchellite are sectile, soft ($H=1\frac{1}{2}$ to 2 on the Mohs scale), and have a perfect {001} cleavage. The best crystal obtained was partially cleaved into two portions, and systematic error introduced in the data by attendant 'splitting' of reflections limited refinement of the structure to $R=14.9\%$ for 1520 independent detectable data. The asymmetric unit of the structure contains four metal and six sulfur atoms. The metal atoms are coordinated by three sulfur atoms to form the trigonal pyramid characteristic of group V metals; the sulfur atoms display polar twofold coordination. The occupancy of the metal sites is disordered. Average metal-sulfur distances for the individual pyramids vary between 2.30 and 2.42 Å, intermediate between usual As-S and Sb-S separations, and in general accord with the occupancy of the site. The structure consists of thick sheets parallel to (001). The simplest structural unit within these sheets is an open, meandering 8-membered ring oriented normal to the plane of the sheet.

Introduction

Getchellite, AsSbS₃, is a recently discovered mineral from Humboldt County, Nevada (Weissberg, 1965). Crystals are dark red, sectile, very soft ($H=1\frac{1}{2}$ to 2 on the Mohs scale), and have a perfect {001} cleavage. Arsenic and antimony sulfides occur in close association in many mineral deposits, and the reason why getchellite, with its distinctive physical properties, had not previously been discovered remains an intriguing question. The only trisulfides which had been previously known in this system are orpiment, As₂S₃, which has a layer structure (Morimoto, 1954; Mullen & Nowacki, 1972), and stibnite, Sb₂S₃, which has a chain structure (Šćavničar, 1960; Bayliss & Nowacki, 1972). The physical properties of getchellite strongly suggest a layer structure, but the lattice constants of the material (Table 1, below) bear no apparent relation to those of orpiment. The present study of getchellite was undertaken to determine its relation to other group V metal sulfides.

Experimental

All naturally occurring crystals of getchellite were found to be badly deformed. The present investigation was therefore conducted with material synthesized hydrothermally from As₃SbS₆ glass maintained at 260°C under 1 kbar pressure. A single crystal suitable for study was obtained only with great difficulty. The material is commonly twinned on (001) and cleaves or plastically deforms upon the slightest mechanical manipulation. The best crystal found was completely free of twinning or deformation, but was partially cleaved. The diffraction spots obtained were therefore slightly

split. This did not preclude a structural investigation but, as noted below, introduced systematic error in the diffraction intensities which were subsequently collected.

Diffraction patterns of getchellite displayed diffraction symmetry $2/m$ and systematic absences for reflections $h0l$ with $h \neq 2n$ and $0k0$ with $k \neq 2n$. The diffraction symbol is thus $2/m P2_1/a$, which unambiguously specifies $P2_1/a$ as the space group. Precise lattice constants were obtained from measurements of back-reflection Weissenberg films. Least-squares refinement of lattice constants and parameters characterizing film shrinkage, sample eccentricity, and absorption was performed with the program *LCLSQ* (Burnham, 1962), using 58 $h0l$ and 28 $hk0$ reflections. The lattice constants obtained, Table 1, are in good agreement with those reported by Weissberg. The present lattice constants provide a density of 3.984 g cm⁻³ for $Z=8$ AsSbS₃ per cell; the density measured for naturally occurring getchellite is 3.29 ± 0.03 g cm⁻³ (Weissberg, 1965).

Table 1. *Lattice constants for AsSbS₃*

	Present work	Weissberg (1965)
a	11.8568 (7) Å	11.85 (2) Å
b	9.0152 (4)	8.99 (2)
c	10.1938 (5)	10.16 (2)
β	116.365 (4)°	116.45 (20)°

The crystal studied was a (001) plate measuring about $0.14 \times 0.14 \times 0.04$ mm ($\mu_{I\max}=4.69$, $\mu_{I\min}=1.34$ for Cu $K\alpha$ radiation). Its shape could be satisfactorily

approximated by $\{001\}$ plus a collection of five additional planar surfaces taken normal to the surface of the plate. It was found that the partial cleavage separating the crystal into two portions resulted in reflections split primarily in φ rather than γ when b was employed as the rotation axis. The splitting affected reflections in the neighborhood of c^* most severely, while the two reflections were nearly superposed in the vicinity of a^* .

Integrated intensities were collected with Ni-filtered Cu $K\alpha$ radiation using an ω scan (stationary counter, rotating crystal) performed with an equi-inclination diffractometer equipped with a proportional counter as detector. The range of the scan in φ was extended

over a wider angular range than usual (as much as 10°) in order to insure integration of reflections from both portions of the split crystal. Background intensity was recorded for 50 sec at both the beginning and termination of each scan. The integrated intensities were corrected for Lorentz, polarization, and absorption factors with the aid of the program *GNABS* (Burnham, 1966). No correction for extinction was made. An intensity was considered to be below the minimum detectable value when $B + 0.6745\sigma_B$ exceeded $E - 0.6745\sigma_E$, where B is the integrated background, E is the total number of counts accumulated, and 0.6745σ is the probable error computed from counting statistics. Of 2317 independent reflections contained within the Cu $K\alpha$ sphere, 1816 were accessible with the diffractometer which was used. Of these, 296 were undetectable on the basis of the above criterion, and were assigned values equal to $\frac{1}{3}$ of the minimum detectable intensity. The measurable data provided 34 observations per parameter in a subsequent refinement with isotropic temperature factors.

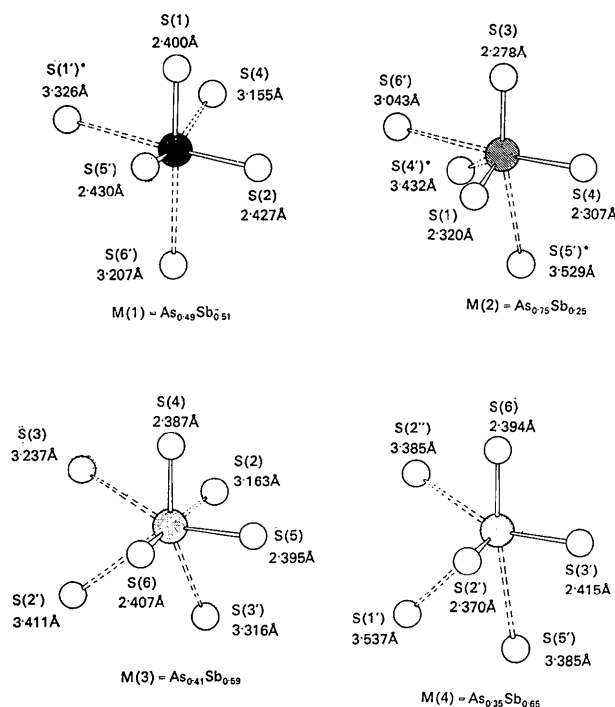


Fig. 1. Metal-atom coordination polyhedra in getchellite showing arrangement of second-nearest sulfur atom neighbors within 3.5 Å. Asterisk denotes an interlayer separation.

Solution and refinement of the structure

The structure was determined by the symbolic addition procedure using the program *MAGIC* (Fleischer, Dewar & Stone, 1967). For the 600 largest E 's ($E > 0.972$), 505 signs were determined, almost all of which subsequently proved to be correct (for example, only one of the 50 largest E 's was incorrectly signed). An E map revealed four large maxima, of which three were of roughly equal magnitude. The two largest were selected as Sb and the remaining pair designated as As. Five maxima of medium weight were readily identified as S atoms. A sixth S atom was selected from among four weak maxima on the basis of interatomic distances.

The full-matrix least-squares program *SFLS5* (Prewitt, 1962) was used for structure factor calculation and refinement. Neutral-atom form factors from *International Tables for X-ray Crystallography* (1962) were used. Corrections for anomalous scattering were used for all atoms. A weighting scheme based upon the standard deviation of F_{obs} (as derived from counting statistics) was used during most stages of refinement. This scheme was modified in the final cycles by an empirical

Table 2. Atomic positions, site occupancies, and temperature factors for getchellite

Estimated standard deviations in parentheses.

	Occupancy (fraction Sb)	x	y	z	B (\AA^2)
M(1)	0.514 (18)	0.1224 (4)	0.3581 (4)	0.1748 (6)	2.93 (12)
M(2)	0.246 (—)*	0.2306 (5)	0.7263 (6)	0.1429 (7)	3.26 (15)
M(3)	0.587 (18)	0.4849 (4)	0.4389 (5)	0.3173 (6)	3.19 (12)
M(4)	0.653 (19)	0.8246 (4)	0.5225 (4)	0.4593 (5)	3.23 (12)
S(1)		0.0710 (13)	0.6147 (13)	0.1805 (16)	2.54 (28)
S(2)		0.2830 (12)	0.3496 (12)	0.4269 (16)	2.53 (28)
S(3)		0.3861 (13)	0.7556 (13)	0.3749 (17)	3.05 (30)
S(4)		0.3179 (13)	0.5191 (13)	0.0913 (17)	3.12 (30)
S(5)		0.4506 (13)	0.1855 (14)	0.2386 (16)	2.75 (29)
S(6)		0.6399 (13)	0.4928 (13)	0.2319 (16)	2.56 (28)

* Dependent occupancy.

Table 3. Observed and calculated structure factors

Columns give, respectively, values of h and l, with corresponding values of F_{obs} and F_{cal}. Unobservable values are indicated by an asterisk; R=14.9% for 1520 observable values.

Table with multiple columns containing h, l, F_obs, and F_cal values. The table is organized into several sections, each with its own header. The data consists of numerical values for structure factors, with some entries marked with an asterisk to indicate unobservable values.

function of F_{obs} which was designed to keep the value of $w(|F_{\text{obs}}| - |F_{\text{cal}}|)^2$ constant and independent of the magnitude of F_{obs} .

Refinement of the model derived from the E map terminated at $R = \sum ||F_{\text{obs}}| - |F_{\text{cal}}|| / \sum |F_{\text{obs}}|$ of 16%. Two anomalies were noted at this point: the temperature factors for the two atoms identified as Sb were much larger (3.4 \AA^2) than those for the atoms designated as As (1.5 \AA^2); further, the Sb-S bond lengths were slightly shorter than normal, while those for As-S were anomalously long. Interchange of the atoms designated as As and Sb failed to improve the situation. Accordingly, we suspected the presence of appreciable disorder among the two types of metal atoms. The full-matrix least-squares program *RFINE* (Finger, 1969) was then

used to refine site occupancies subject to the constraints that (a) the number of atoms distributed over the four metal sites total 2As and 2Sb, and (b) the Sb+As occupancy of each site equals unity. Large correlations of temperature factors with site occupancies were encountered, as expected, but it was found that convergence to roughly the same occupancies (within 0.7σ to 2.0σ) for the four sites resulted regardless of whether the initial distribution of atoms was taken to be complete order, complete disorder, or a set of occupancies derived on the basis of interatomic distances.

Throughout these stages of refinement it was noted that the agreement between F_{obs} and F_{cal} was markedly poorer for high-angle reflections. Similarly, the value of R increased rapidly for the higher levels of the recip-

Table 4. *Bond lengths and angles in getchellite*

Estimated standard deviations in parentheses; second nearest neighbors within 3.5 \AA are enclosed by brackets and designated by an asterisk if an interlayer separation.

Metal polyhedra			
M(1) $\text{As}_{0.49}\text{Sb}_{0.51}$			
M(1)-S(1)	2.400 (13) \AA	S(5')-S(1)	3.235 (19) \AA
M(1)-S(2)	2.427 (15)	S(2)-S(5')	3.549 (19)
M(1)-S(5')	2.430 (16)	S(1)-S(2)	3.568 (18)
Average	2.419		
[S(4)]	3.155 (16)]	S(5')-M(1)-S(1)	84.1 (5) $^\circ$
[S(6')]	3.207 (12)]	S(2)-M(1)-S(5')	93.9 (5)
[S(1')]	3.326 (15)]*	S(1)-M(1)-S(2)	95.3 (5)
		Average	91.1
M(2) $\text{As}_{0.75}\text{Sb}_{0.25}$			
M(2)-S(3)	2.278 (15) \AA	S(3)-S(4)	3.388 (21) \AA
M(2)-S(4)	2.307 (14)	S(4)-S(1)	3.536 (21)
M(2)-S(1)	2.320 (16)	S(1)-S(3)	3.595 (19)
Average	2.302		
[S(6')]	3.043 (14)]	S(3)-M(2)-S(4)	95.3 (5) $^\circ$
[S(4')]	3.432 (15)]*	S(4)-M(2)-S(1)	99.7 (5)
[S(5')]	3.529 (16)]*	S(1)-M(2)-S(3)	102.8 (6)
		Average	99.3
M(3) $\text{As}_{0.41}\text{Sb}_{0.59}$			
M(3)-S(4)	2.387 (15) \AA	S(4)-S(5)	3.417 (18) \AA
M(3)-S(5)	2.395 (13)	S(6)-S(4)	3.439 (20)
M(3)-S(6)	2.407 (16)	S(5)-S(6)	3.585 (19)
Average	2.396		
[S(2)]	3.163 (15)]	S(4)-M(3)-S(5)	91.2 (5) $^\circ$
[S(3)]	3.237 (13)]	S(6)-M(3)-S(4)	91.7 (5)
[S(3')]	3.316 (16)]	S(5)-M(3)-S(6)	96.6 (15)
[S(2')]	3.411 (13)]	Average	93.2
M(4) $\text{As}_{0.35}\text{Sb}_{0.65}$			
M(4)-S(2')	2.370 (15) \AA	S(3')-S(6)	3.466 (18) \AA
M(4)-S(6)	2.394 (14)	S(6)-S(2')	3.482 (20)
M(4)-S(3')	2.415 (14)	S(2')-S(3')	3.524 (22)
Average	2.393		
[S(2'')]	3.385 (12)]	S(3')-M(4)-S(6)	92.2 (5) $^\circ$
[S(5')]	3.385 (14)]	S(6)-M(4)-S(2')	93.9 (5)
[S(1')]	3.537 (15)]	S(2')-M(4)-S(3')	94.9 (5)
		Average	93.7
Sulfur bond angles		Interlayer separations less than 4 \AA	
M(1)-S(2)-M(4)	99.4 (5) $^\circ$	M(1)-S(1')	3.326 (15) \AA
M(1)-S(1)-M(2)	100.3 (6)	M(2)-S(4')	3.432 (15)
M(3)-S(6)-M(4)	100.9 (6)	M(2)-S(5')	3.529 (16)
M(1)-S(5)-M(3)	101.9 (5)	S(4)-S(6')	3.547 (23)
M(2)-S(3)-M(4)	103.5 (5)	S(4)-S(5')	3.766 (19)
M(2)-S(4)-M(3)	106.8 (6)	S(1)-S(1')	3.892 (28)
Average	102.1		

rocal lattice. We interpreted this effect as being due largely to a systematic error in the data introduced by the increased amount of splitting present in the high-angle reflections. Accordingly, additional refinement of atomic coordinates and site occupancies was performed using 741 low-angle reflections (providing 17 observations per parameter). Refinement terminated for this subset of reflections at $R=13.3\%$ and a 'weighted' R , that is $\{\sum w(|F_{\text{obs}}| - |F_{\text{cal}}|)^2 / \sum w F_{\text{obs}}^2\}^{1/2}$, of 14.8% . For all 1520 observable reflections R and the weighted R were 14.9 and 17.1% respectively. Upon inclusion of the 296 unobserved data, R increased to 16.3% .

An attempt was also made to include anisotropic temperature factor coefficients in the refinement. This incorporation produced an improved value of R (10.6% for the low-angle data), but the deviation from isotropic thermal motion acquired for all atoms was of the same sort: mainly an increase in the value of β_{33} . Such anisotropy was physically unreasonable and, since reflections were most noticeably split in the vicinity of c^* , was interpreted as another indication of systematic error present in the data.

Results of the refinement

The asymmetric unit of getchellite contains 4 metal atoms and 6 sulfur atoms. All atoms are located at a general position of the space group. The atomic positions, metal site occupancies, and isotropic temperature factors are presented in Table 2. The observed structure factors are compared in Table 3 with values computed from the parameters of Table 2.

Discussion of the structure

Of the four metal atom sites in getchellite, M(1) and M(3) contain approximately equal amounts of As and

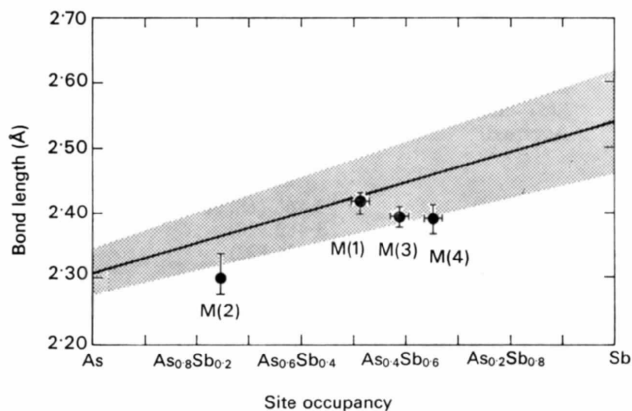


Fig. 2. Average metal-sulfur separation for the MS_3 trigonal pyramids in getchellite as a function of metal-site occupancy. As-S and Sb-S separations are average bridging bond-lengths after Takéuchi & Sadanaga (1969). Shaded band is r.m.s. deviation from mean. (Vertical bar is total range of bond lengths occurring within a polyhedron; horizontal bar is estimated standard deviation of site occupancy.)

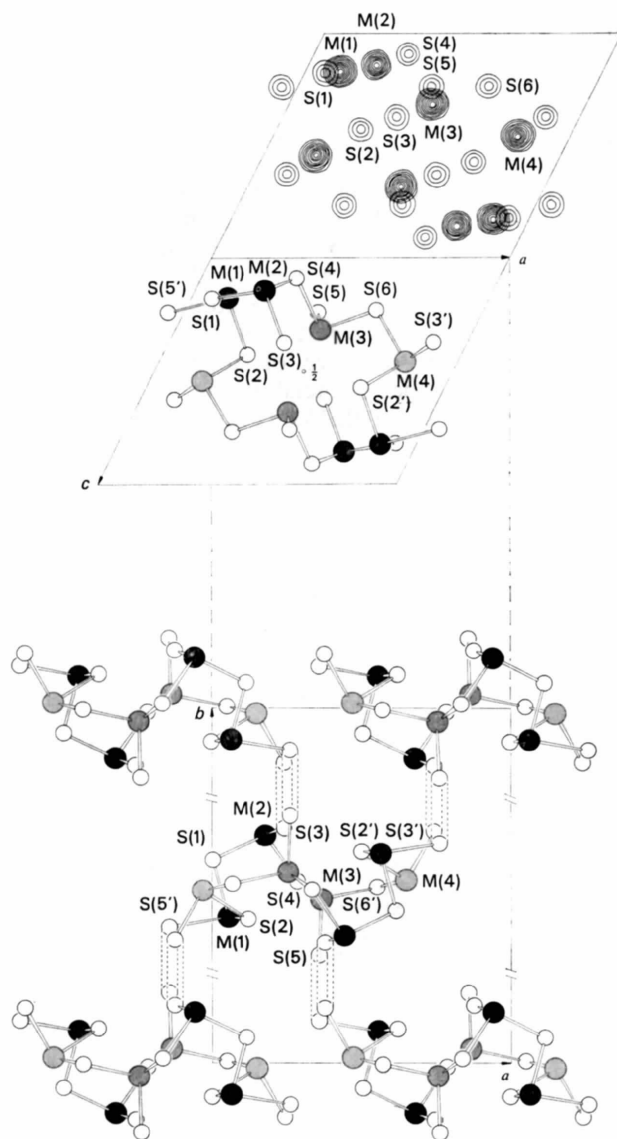


Fig. 3. Projections of the eight-membered $(\text{As,Sb})_8\text{S}_{16}$ ring contained in getchellite. (a) Projection along b , and composite of electron-density sections through the atoms. Contour interval $10 \text{ e } \text{Å}^{-3}$; zero contour omitted. Note that all metal sites contain comparable numbers of electrons. (b) 'Exploded' projection of the structure along c^* (i.e., normal to the plane of layers) illustrating linkage of eight-membered rings.

Sb, M(4) contains a slight excess of Sb, while M(2) consists mainly of As. Upon taking the disorder into account, all metal atoms acquired virtually identical temperature factors. All metal sites are three-coordinated by S, the MS_3 units forming trigonal pyramids. This is the coordination found in most arsenic sulfosalts and in orpiment, As_2S_3 (Morimoto, 1954; Mullen & Nowacki, 1972). Only half the Sb in stibnite, Sb_2S_3 (Šćavničar, 1960; Bayliss & Nowacki, 1972), show this

coordination. The other half, as well as the Sb in nearly all antimony sulfosalts, exhibit five-coordination (square-pyramidal). A fourth and fifth orthogonal bond (and, indeed, a sixth for M(1), which has nearly octahedral coordination) may be found among the more distant neighbors in each metal atom polyhedron, Fig. 1. These bonds, however, are much larger than those usually encountered in SbS_5 groups, and are comparable to van der Waals separations (3.85 Å for As-S, and 4.05 for Sb-S). All S atoms have a polar twofold coordination similar to that found in orpiment and the ring molecules of elemental sulfur (Abrahams, 1955; Donohue, Caron & Goldish, 1961).

Bond angles and lengths are summarized in Table 4. The metal-sulfur bond lengths are, as expected, found to be intermediate between the average bridging As-S (2.31 Å) and Sb-S (2.54 Å) distances found in sulfosalts (Takéuchi & Sadanaga, 1969), and are consistent with the occupancy of the sites, Fig. 2. The shortest bond length observed, M(2)-S(3), involves the metal site which has the highest As content. It is interesting to speculate whether the disorder is a consequence of the crystals having been a synthetic product. Naturally occurring crystals of getchellite, grown over extended periods of time, might well be ordered.

The structure of getchellite consists of sheets equal to d_{001} in thickness (9.13 Å), which are parallel to (001), the cleavage and twin plane of the structure. Within each layer, the structure is an open and meandering glass-like network. The simplest structural group is a puckered 8-membered ring of symmetry $\bar{1}$, parallel to (010). One such ring is shown in Fig. 3(a). These rings are not linked to any neighboring rings in the same (010) plane. Each ring is instead linked to two others above and two below, each related to it by the a glide [Fig. 3(b)].

The structure of getchellite appears to be unrelated to that of either stibnite or orpiment. While orpiment is also a sheet structure, it consists of 6-membered rings parallel to the plane of the sheets, and linked to form an essentially two-dimensional layer. The 8-membered rings in getchellite are instead normal to the plane of the layers and stacked above one another.

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The Crystal Structure of Hureaulite, $Mn_5(HOPO_3)_2(PO_4)_2(H_2O)_4$

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Hureaulite is monoclinic $C2/c$ with $Z=4$ and cell dimensions $a=17.66$ (2), $b=9.123$ (2), $c=9.498$ (2) Å and $\beta=96.58$ (2)°. Three-dimensional data were collected with a Weissenberg camera (Cu $K\alpha$ radiation). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares analysis to an R index of 0.053 for 1116 observed reflexions. The structure consists of PO_4 and $HOPO_3$ tetrahedra, linked together by a hydrogen bond, and by groups of five edge-shared Mn octahedra. The hydrogen atom positions were determined from a difference synthesis. On the basis of the structure determination and according to the chemical analysis, the crystal-chemical formula for the specimen studied is $(Mn_{4.34}, Fe_{0.55}, Mg_{0.07}, Ca_{0.04})(HOPO_3)_2(PO_4)_2(H_2O)_4$.

Introduction

Hureaulite was first described by Alluaud (1826). The main physical and chemical properties are given in

Dana's System of Mineralogy (Palache, Berman & Frondel, 1951). The structure determination of hureaulite was undertaken in order to define the crystal-chemical formula and the structural role played by the