

## The Crystal Structure of Fülöppite, $\text{Pb}_3\text{Sb}_8\text{S}_{15}$

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Fülöppite,  $\text{Pb}_3\text{Sb}_8\text{S}_{15}$ , from the type locality in Nagybánya, Romania, is monoclinic  $C2/c$  with  $a = 13.441$  (15),  $b = 11.726$  (15),  $c = 16.930$  (15) Å,  $\beta = 94.71$  (8)°;  $D_{\text{meas}} = 5.22$ ,  $D_{\text{calc}} = 5.19$  g cm<sup>-3</sup>;  $Z = 4$ . The structure was solved from 1568 'observed' ( $F_o^2 \geq 5\sigma F_o^2$ ) symmetry-independent reflexions collected on a Picker four-circle FACS-1 diffractometer using Mo  $K\alpha$  ( $\lambda = 0.71069$  Å) radiation. Absorption corrections were applied to the data and the structure was refined by full-matrix least-squares calculations with anisotropic temperature factors to an  $R$  value of 6.07% ( $R_w = 8.01\%$ ). The structure can be resolved into two kinds of interleaving and interlocked Pb-Sb-S complex, both of which extend parallel to [110]. The first kind, of composition  $\text{Pb}_2\text{Sb}_4\text{S}_6$ , is similar to the groups that form the chains in stibnite ( $\text{Sb}_2\text{S}_3$ ) but have Pb bonded to both ends. The second kind has the composition  $\text{PbSb}_4\text{S}_9$  and consists of a string of four  $\text{SbS}_3$  polyhedra symmetrically arranged about a central twofold rotation axis and a Pb atom. Three of the four Sb atoms have three 'close' (2.43–2.56 Å) S neighbours; the other has five (2.48–3.14 Å). The two Pb atoms are irregularly coordinated by six and seven S atoms at distances of 2.76 to 3.32 Å.

### Introduction

Fülöppite is a member of a group of four mineral sulphosalts with progressive chemical compositions that can be expressed as  $\text{Pb}_{3+2n}\text{Sb}_8\text{S}_{15+2n}$  in which  $n = 0$  to 3. Two cell constants,  $a$  and  $b$  remain invariant at  $13.5 \pm 0.1$  and  $11.8 \pm 0.1$  Å, respectively, while  $c$  increases with increasing Pb content (Table 1). The increase in  $c$  is not systematic and the values of  $\beta$  are neither constant (except for plagionite and semseyite) nor progressive but, as Jambor (1969) has noted, the parameter  $c \sin \beta$  changes regularly and thus the systematic increase in calculated density with increase in Pb shown by the table, is to be expected.

The crystal structures of plagionite and semseyite have been solved, respectively, by Cho & Wuensch (1970) and Kohatsu & Wuensch (1974). The space group is  $C2/c$  for both structures. The systematically absent reflexions which have been recorded for the other two members of the group are in accord with  $C2/c$ .

### Experimental

Crystals of fülöppite are rare. Specimens from Romania, which have provided the best material, are usually less than a millimetre in diameter and irreg-

ularly intergrown and intimately associated with other minerals. The faces are typically curved, striated and dull. The crystals are, therefore, generally unsuitable for structural studies and the search for a crystal bounded by measurable faces or one suitable for grinding into a sphere had to be abandoned. The crystal selected for the present study is an oddly shaped fragment from Nagybánya, Romania (Royal Ontario Museum *M* 19239) measuring approximately  $0.23 \times 0.11 \times 0.14$  mm in the  $a$ ,  $b$  and  $c$  directions. Only one face, later identified as (00 $\bar{1}$ ), gave a distinct signal on an optical two-circle goniometer although two small striated zones were detected with a microscope under high magnification. But in contrast to most of the material, it gave sharp X-ray reflexions. The crystal was mounted to rotate about [010]. A series of Weissenberg and precession films established that the systematically absent reflexions are in agreement with the space group  $C2/c$  as previously reported.

The cell parameters were calculated from the measurement of selected high-order  $h00$ ,  $0k0$  and  $00l$   $2\theta$  angles, and the angle between the  $a^*$  and  $c^*$  rows on a Picker four-circle FACS-1 diffractometer. The parameters  $a = 13.441$  (15),  $b = 11.726$  (15),  $c = 16.930$  (15) Å;  $\beta = 94.71$  (8)° are in substantial agreement with previous values. The calculated density for the cell contents  $4[\text{Pb}_3\text{Sb}_8\text{S}_{15}]$  is  $5.19$  g cm<sup>-3</sup> compared with  $5.22$

Table 1. *The plagionite group*

		$c$	$\beta$	$c \sin \beta$	$D_m$	$D_c$	Reference
Fülöppite	$\text{Pb}_3\text{Sb}_8\text{S}_{15}$	16.930	94.71	16.87	5.22	5.19	1
Plagionite	$\text{Pb}_5\text{Sb}_8\text{S}_{17}$	19.9834	107.17	19.09	5.54	5.55	2
Heteromorphite	$\text{Pb}_7\text{Sb}_8\text{S}_{19}$	21.22	90.83	21.22	5.73	5.86	3
Semseyite	$\text{Pb}_9\text{Sb}_8\text{S}_{21}$	24.435	106.047	23.48	6.03	6.12	4

References: (1) Nuffield (1946) and this study; (2) Nuffield & Peacock (1945), Cho & Wuensch (1970); (3) Dana & Dana (1944), Jambor (1969); (4) Nuffield & Peacock (1945), Kohatsu & Wuensch (1974).

measured (Nuffield, 1945). The linear absorption coefficient for Mo  $K\alpha$  ( $\lambda = 0.71069 \text{ \AA}$ ) is  $267.9 \text{ cm}^{-1}$ .

The intensity data were collected on the Picker diffractometer with filtered Mo  $K\alpha$  radiation in the  $\theta/2\theta$  scan mode to  $50^\circ$  in  $2\theta$ . A scan rate of  $1^\circ \text{ min}^{-1}$  with a 20 s background count on either side of the peak was employed. A standard reflexion, monitored at 50-reflexion intervals, showed a maximum deviation of about 5.5% from the median and was used to place the data on a uniform scale. 2411 symmetry-independent reflexions were measured of which 1568 had  $|F^2| \geq 5\sigma F^2$  and were treated as observed. In addition  $\varphi$  sweeps were made at  $10^\circ$  intervals over the scan range ( $90\text{--}270^\circ \varphi$ ) for the reflexions 040, 060, 0, 10, 0 and 0, 16, 0 for use in deriving absorption corrections. The data were reduced in the usual way. Absorption corrections were made in the late stages of the refinement.

### Determination and refinement of the structure

An analysis of the distribution of  $E$  values indicated the centrosymmetric space group  $C2/c$  rather than  $Cc$ :

$$\begin{array}{ll} \text{av. } |E^2| & = 1.00 & |E| > 1 = 30.4\% \\ \text{av. } |E^2 - 1| & = 0.89 & |E| > 2 = 3.9 \\ \text{av. } |E| & = 0.85 & |E| > 3 = 0.3. \end{array}$$

A set of the 224 largest ( $E \geq 1.85$ ) normalized structure factors was used in a direct determination of the metal positions with the aid of the *TANFOR* (Drew & Larson, 1968) program. One of the iterations assigned phases to all 224 reflexions and yielded an  $R$  (Karle) value of 12%. An  $E$  map calculated for this solution revealed all the metal positions – two for Pb and four for Sb. A Fourier synthesis, based on  $F_o - F_c$  coefficients for the 1568 ‘observed’ reflexions, gave the S positions. After introduction of corrections for anomalous dispersions and conversion to anisotropic temperature factors, the agreement index  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  reached a value of 0.116 for the ‘observed’ reflexions following several cycles of least-squares refinement using unit weights.

Absorption corrections were effected with the *DATRED* (Fawcett, 1970) program which included the sub-routine *ABSORP* (Coppens, Leiserowitz & Rabinovich, 1965). To obtain bounding plane data for the essentially anhedral crystal of fülöppite, the fragment was mounted on a two-circle device and its surface resolved, under a stereomicroscope, into nine bounding planes of which three consisted of faces [the (00 $\bar{1}$ ) face and the two striated zones mentioned above] and six represented the broken areas. The distance of each plane from a common centre was estimated with a micrometer eyepiece. Spherical coordinates  $\varphi$  and  $\varrho$  (de Jong, 1959) were read for each plane and used to prepare a gnomonic projection from which Miller indices were assigned to the planes. The (00 $\bar{1}$ ) face served as a reference plane to relate the coordinates to the corresponding Picker angles. Table 2 gives the observed and corrected intensities for the 040 reflexions at  $20^\circ$  intervals of  $\varphi$  and indicates the degree of success of the procedure. The variations in intensity that remain are due in part to the errors inherent in averaging broken surfaces as imaginary planes and in setting the planes into a chosen reference orientation for the purpose of reading the spherical coordinates.

Table 2. Net intensities of the 040 reflexions before and after correcting the observed data for shape and size of the crystal

$\varphi$	$I_{\text{uncorr}}$	$I_{\text{corr}}$
$90^\circ$	2618	7987
110	4725	9635
130	6971	10526
150	8966	11355
170	9309	11690
190	8764	10760
210	7203	9593
230	5121	8596
250	3457	9299
270	2659	8113

The absorption corrections obtained with the sub-routine for the four kinds of  $0k0$  reflexion in the  $\varphi$

Table 3. Fractional coordinates ( $\times 10^5$ ), anisotropic ( $\times 10^5, \text{\AA}^2$ ) and isotropic ( $\text{\AA}^2$ ) thermal parameters

The temperature factor has the form  $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .  $B$  values are from the final cycle of isotropic refinement. E.s.d.'s are in parentheses and were obtained from the last cycle of refinement.

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$B$
Pb(1)	0	37137 (17)	25	347 (12)	235 (14)	108 (7)	0	95 (7)	0	1.65 (4)
Pb(2)	30719 (9)	42895 (12)	33253 (9)	192 (7)	300 (10)	157 (5)	-27 (7)	47 (4)	3 (6)	1.56 (3)
Sb(1)	37263 (14)	13632 (18)	49484 (13)	92 (10)	191 (15)	95 (8)	-35 (10)	44 (7)	11 (8)	0.91 (4)
Sb(2)	40863 (15)	17955 (18)	15600 (12)	114 (10)	156 (15)	73 (7)	-16 (10)	31 (6)	7 (8)	0.80 (4)
Sb(3)	8902 (15)	4903 (19)	41560 (14)	132 (11)	197 (17)	146 (9)	-82 (10)	2 (7)	58 (9)	1.19 (5)
Sb(4)	14000 (14)	25122 (18)	6034 (12)	67 (10)	168 (15)	56 (7)	21 (9)	23 (6)	-25 (8)	0.67 (4)
S(1)	35660 (60)	4863 (71)	25578 (51)	203 (41)	238 (61)	114 (29)	22 (41)	32 (27)	18 (33)	1.45 (16)
S(2)	5000	31669 (94)	25000	161 (57)	103 (72)	113 (40)	0	-34 (36)	0	1.03 (20)
S(3)	26624 (52)	2731 (63)	3609 (47)	101 (35)	91 (48)	110 (28)	16 (35)	66 (25)	50 (30)	0.84 (14)
S(4)	18550 (57)	24606 (71)	39631 (53)	140 (40)	201 (58)	182 (33)	-40 (39)	83 (28)	-78 (37)	1.35 (15)
S(5)	46720 (54)	36518 (67)	46177 (69)	138 (39)	173 (54)	115 (29)	24 (39)	68 (27)	-35 (33)	0.97 (14)
S(6)	2975 (53)	41679 (61)	8294 (44)	135 (36)	44 (46)	65 (25)	-2 (34)	36 (23)	2 (29)	0.61 (13)
S(7)	7034 (54)	13327 (67)	16400 (49)	122 (37)	179 (53)	104 (27)	23 (38)	43 (25)	17 (33)	0.93 (14)
S(8)	27204 (53)	32013 (66)	15967 (48)	109 (39)	130 (52)	142 (31)	38 (37)	-57 (26)	2 (33)	1.07 (15)



Table 5 (cont.)

Apex atom Sb(3)			Apex atom S(4)		
S(3 <sup>iv</sup> )	S(4 <sup>i</sup> )	88.6°	Pb(1 <sup>i</sup> )	Pb(2 <sup>i</sup> )	80.1°
S(3 <sup>iv</sup> )	S(5 <sup>v</sup> )	91.6	Pb(1 <sup>i</sup> )	Sb(1 <sup>i</sup> )	168.8
S(3 <sup>iv</sup> )	S(5 <sup>vi</sup> )	80.7	Pb(1 <sup>i</sup> )	Sb(1 <sup>iv</sup> )	92.3
S(3 <sup>iv</sup> )	S(7 <sup>iii</sup> )	169.8	Pb(1 <sup>i</sup> )	Sb(3 <sup>i</sup> )	96.8
S(3 <sup>iv</sup> )	S(8 <sup>vii</sup> )	68.0	Pb(2 <sup>i</sup> )	Sb(1 <sup>i</sup> )	92.7
S(4 <sup>i</sup> )	S(5 <sup>v</sup> )	167.9	Pb(2 <sup>i</sup> )	Sb(1 <sup>iv</sup> )	94.9
S(4 <sup>i</sup> )	S(5 <sup>vi</sup> )	86.3	Pb(2 <sup>i</sup> )	Sb(3 <sup>i</sup> )	163.2
S(4 <sup>i</sup> )	S(7 <sup>iii</sup> )	89.7	Sb(1 <sup>i</sup> )	Sb(1 <sup>iv</sup> )	96.9
S(4 <sup>i</sup> )	S(8 <sup>vii</sup> )	109.4	Sb(1 <sup>i</sup> )	Sb(3 <sup>i</sup> )	87.5
S(5 <sup>v</sup> )	S(5 <sup>vi</sup> )	81.7	Sb(1 <sup>iv</sup> )	Sb(3 <sup>i</sup> )	101.8
S(5 <sup>v</sup> )	S(7 <sup>iii</sup> )	87.9			
S(5 <sup>v</sup> )	S(8 <sup>vii</sup> )	81.9			
S(5 <sup>vi</sup> )	S(7 <sup>iii</sup> )	89.2			
S(5 <sup>vi</sup> )	S(8 <sup>vii</sup> )	144.0			
S(7 <sup>iii</sup> )	S(8 <sup>vii</sup> )	121.9			
Apex atom Sb(4)			Apex atom S(5)		
S(3 <sup>i</sup> )	S(3 <sup>vi</sup> )	110.5°	Pb(2 <sup>i</sup> )	Sb(1 <sup>i</sup> )	93.9°
S(3 <sup>i</sup> )	S(5 <sup>viii</sup> )	87.2	Pb(2 <sup>i</sup> )	Sb(2 <sup>iii</sup> )	94.9
S(3 <sup>i</sup> )	S(6 <sup>i</sup> )	175.3	Pb(2 <sup>i</sup> )	Sb(3 <sup>v</sup> )	90.3
S(3 <sup>i</sup> )	S(7 <sup>i</sup> )	82.4	Pb(2 <sup>i</sup> )	Sb(3 <sup>vi</sup> )	104.9
S(3 <sup>i</sup> )	S(8 <sup>i</sup> )	89.8	Pb(2 <sup>i</sup> )	Sb(4 <sup>viii</sup> )	164.3
S(3 <sup>vi</sup> )	S(5 <sup>viii</sup> )	112.1	Sb(1 <sup>i</sup> )	Sb(2 <sup>iii</sup> )	77.3
S(3 <sup>vi</sup> )	S(6 <sup>i</sup> )	74.0	Sb(1 <sup>i</sup> )	Sb(3 <sup>v</sup> )	167.1
S(3 <sup>vi</sup> )	S(7 <sup>i</sup> )	162.2	Sb(1 <sup>i</sup> )	Sb(3 <sup>vi</sup> )	92.5
S(3 <sup>vi</sup> )	S(8 <sup>i</sup> )	78.6	Sb(1 <sup>i</sup> )	Sb(4 <sup>viii</sup> )	79.4
S(5 <sup>viii</sup> )	S(6 <sup>i</sup> )	89.8	Sb(2 <sup>iii</sup> )	Sb(3 <sup>v</sup> )	90.1
S(5 <sup>viii</sup> )	S(7 <sup>i</sup> )	79.8	Sb(2 <sup>iii</sup> )	Sb(3 <sup>vi</sup> )	158.3
S(5 <sup>viii</sup> )	S(8 <sup>i</sup> )	169.3	Sb(2 <sup>iii</sup> )	Sb(4 <sup>viii</sup> )	69.8
S(6 <sup>i</sup> )	S(7 <sup>i</sup> )	93.6	Sb(3 <sup>v</sup> )	Sb(3 <sup>vi</sup> )	98.3
S(6 <sup>i</sup> )	S(8 <sup>i</sup> )	92.5	Sb(3 <sup>v</sup> )	Sb(4 <sup>viii</sup> )	93.4
S(7 <sup>i</sup> )	S(8 <sup>i</sup> )	89.6	Sb(3 <sup>vi</sup> )	Sb(4 <sup>viii</sup> )	89.7
Apex atom Pb(1)			Apex atom S(6)		
S(1 <sup>v</sup> )	S(1 <sup>vii</sup> )	86.0°	Pb(1 <sup>i</sup> )	Sb(1 <sup>vii</sup> )	129.1°
S(1 <sup>v</sup> )	S(6 <sup>i</sup> )	92.7 (× 2)	Pb(1 <sup>i</sup> )	Sb(1 <sup>viii</sup> )	110.2
S(1 <sup>v</sup> )	S(6 <sup>iii</sup> )	71.8 (× 2)	Pb(1 <sup>i</sup> )	Sb(2 <sup>v</sup> )	74.6
S(1 <sup>v</sup> )	S(7 <sup>i</sup> )	148.0 (× 2)	Pb(1 <sup>i</sup> )	Sb(4 <sup>i</sup> )	97.8
S(1 <sup>v</sup> )	S(7 <sup>iii</sup> )	112.4 (× 2)	Sb(1 <sup>vii</sup> )	Sb(1 <sup>viii</sup> )	107.5
S(6 <sup>i</sup> )	S(6 <sup>iii</sup> )	159.1	Sb(1 <sup>vii</sup> )	Sb(2 <sup>v</sup> )	71.3
S(6 <sup>i</sup> )	S(7 <sup>i</sup> )	70.4 (× 2)	Sb(1 <sup>vii</sup> )	Sb(4 <sup>i</sup> )	107.0
S(6 <sup>i</sup> )	S(7 <sup>iii</sup> )	129.8 (× 2)	Sb(1 <sup>viii</sup> )	Sb(2 <sup>v</sup> )	91.9
S(7 <sup>i</sup> )	S(7 <sup>iii</sup> )	65.6	Sb(1 <sup>viii</sup> )	Sb(4 <sup>i</sup> )	101.2
			Sb(2 <sup>v</sup> )	Sb(4 <sup>i</sup> )	166.6
Apex atom Pb(2)			Apex atom S(7)		
S(1 <sup>vii</sup> )	S(3 <sup>vii</sup> )	84.7°	Pb(1 <sup>i</sup> )	Pb(2 <sup>vii</sup> )	150.0°
S(1 <sup>vii</sup> )	S(4 <sup>i</sup> )	96.9	Pb(1 <sup>i</sup> )	Sb(3 <sup>iii</sup> )	106.9
S(1 <sup>vii</sup> )	S(5 <sup>i</sup> )	161.6	Pb(1 <sup>i</sup> )	Sb(4 <sup>i</sup> )	88.8
S(1 <sup>vii</sup> )	S(7 <sup>vii</sup> )	90.9	Pb(2 <sup>vii</sup> )	Sb(3 <sup>iii</sup> )	97.9
S(1 <sup>vii</sup> )	S(8 <sup>i</sup> )	71.0	Pb(2 <sup>vii</sup> )	Sb(4 <sup>i</sup> )	103.2
S(3 <sup>vii</sup> )	S(4 <sup>i</sup> )	76.3	Sb(3 <sup>iii</sup> )	Sb(4 <sup>i</sup> )	100.7
S(3 <sup>vii</sup> )	S(5 <sup>i</sup> )	78.5			
S(3 <sup>vii</sup> )	S(7 <sup>vii</sup> )	83.0			
S(3 <sup>vii</sup> )	S(8 <sup>i</sup> )	150.5			
S(4 <sup>i</sup> )	S(5 <sup>i</sup> )	86.5			
S(4 <sup>i</sup> )	S(7 <sup>vii</sup> )	157.1			
S(4 <sup>i</sup> )	S(8 <sup>i</sup> )	90.0			
S(5 <sup>i</sup> )	S(7 <sup>vii</sup> )	79.7			
S(5 <sup>i</sup> )	S(8 <sup>i</sup> )	127.3			
S(7 <sup>vii</sup> )	S(8 <sup>i</sup> )	112.9			
Apex atom S(8)					
Pb(2 <sup>i</sup> )	Sb(2 <sup>i</sup> )	103.6°			
Pb(2 <sup>i</sup> )	Sb(3 <sup>vii</sup> )	89.1			
Pb(2 <sup>i</sup> )	Sb(4 <sup>i</sup> )	142.8			
Sb(2 <sup>i</sup> )	Sb(3 <sup>vii</sup> )	94.7			
Sb(2 <sup>i</sup> )	Sb(4 <sup>i</sup> )	104.9			
Sb(3 <sup>vii</sup> )	Sb(4 <sup>i</sup> )	111.7			

## Discussion of the structure

The Sb atoms are surrounded by six [seven in the case of Sb(2)] S atoms within a radius of 4.0 Å in a distorted but readily recognizable octahedral arrangement. The distances vary from 2.428 to 3.742 Å (Table 4) as compared to 4.05 Å for the sum of the van der Waals radii for Sb and S (Evans, 1964). The coordination in stibnite ( $Sb_2S_3$ ) is similar, both kinds of Sb atom being surrounded by seven S atoms at distances ranging from 2.455 to 3.642 Å (Table 7). Bayliss & Nowacki (1972), who have recently refined the structure, describe the Sb(1) atom of stibnite as trivalent and Sb(2) as quintivalent on the basis of the number of 'close' S neighbours. A comparison of Tables 4 and 7 shows that the coordination of S about Sb(1), Sb(2) and Sb(4) in fülöppite resembles the Sb(1) polyhedron in stibnite while the arrangement around Sb(3) is similar to Sb(2) in stibnite.

The coordination about Pb, as in most sulphosalts, is irregular. Pb(1), which occupies the special position 4(e2), has six S neighbours at distances ranging from

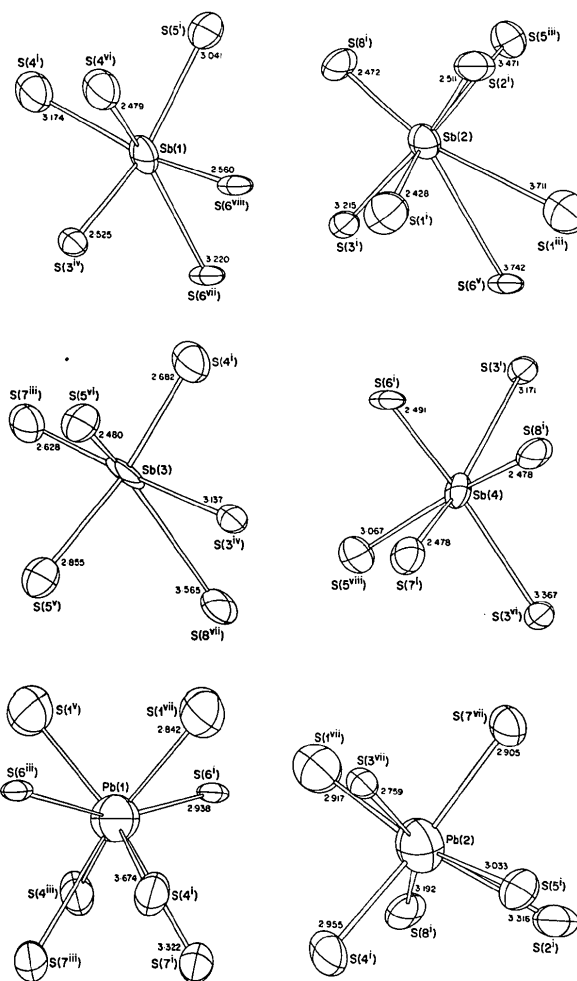


Fig. 1. ORTEP plots of metal-S polyhedra showing anisotropic thermal vibrations of the atoms drawn with 90% probability.





groups along [110] are separated by metal-S distances: Sb(1)-S(4)=3.174, Sb(3)-S(3)=3.137, Pb(2)-S(5)=3.033 Å.

Table 8. Sb-S distances in the  $Pb_2Sb_4S_6$  complexes and in stibnite chains

Fülöppite		Stibnite	
Sb(1)	2.479 Å	Sb(1)	2.521 Å
	2.525		2.539
	3.041		3.111
Sb(3)	2.480	Sb(2)	2.455
	2.682		2.678
	2.855		2.854

The second kind of group consists of a string of four  $SbS_3$  polyhedra [two Sb(2) and two Sb(4) atoms] symmetrically arranged about a central twofold rotation axis and a Pb(1) atom. The group has the composition  $PbSb_4S_9$ . Actually the strings include, at either end, the Sb(1) atoms of the groups of the first kind linked by an Sb-S bond of length 2.560 Å. If the concept of the group is expanded to include the Sb(1) atoms and their coordinating S atoms, the group is comprised of all the trivalent Sb atoms and their three closest S neighbours and has the composition  $PbSb_6S_{13}$ . Sb(1) links the two kinds of group by being a part of both. Pb(2) forms another type of link between the two groups and between groups of the second kind. Pb(1) is the only other metal atom that plays an important role in binding groups of the second kind.

A discussion of the relation between the structure of fülöppite and the structures of pligionite and semseyite must necessarily wait on the publication of more complete accounts than are now available in the literature.

I am indebted to my colleague, Dr Vladimir Kocman, for preparing the *ORTEP* plots and for valuable assistance in collecting and treating the data. Professor B. J. Wuensch provided me with a copy of a forthcoming paper on the structure of pligionite and this aided materially in understanding the structure of

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