Structural principles and classification of sulfosalts

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(Received 12 May 1969)

Abstract

A survey on the dimensions of the TS₅ anionic groups in sulfosalts was carried out, where T represents a trivalent atom such as As, Sb or Bi. The average lengths of T−S non-bridge bonds and S−T−S bridge bonds are respec-
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Introduction

Sulfosalts comprise a group of minerals having the general formula $A_m T_n X_p$, in which the common elements are: as $A$: Ag, Cu, Pb; as $T$: As, Sb, Bi; as $X$: S (BERRY and MASON, 1959)\(^1\), and they can be regarded as salts of the sulfo-acids of trivalent arsenic, antimony or bismuth. In the crystal structures of these minerals, the trivalent atom $T$ is coordinated by three sulfur atoms to form a low pyramid, with $T$ at the vertex and three sulfur atoms at the basal corners. Such pyramids often constitute a complex group, finite or infinite, by sharing sulfur atoms; the independent pyramids or the complex groups are linked together by monovalent atoms such as Ag and Cu or divalent atoms such as Pb or by both kinds. The presence of the TS$_3$ pyramids in the structure is, in fact, the feature that distinguishes a sulfosalt from a sulfide. For example, enargite might, at a glance, be thought, from its composition Cu$_3$AsS$_4$, to be a sulfosalt, but arsenic in

\(^1\) BERRY and MASON have given the general formula $A_m B_n C_p$. However B is here replaced by $T$ simply to avoid confusion with boron.
this compound is pentavalent and takes a tetrahedral coordination of sulfur atoms, thus exhibiting the aspect of a derivative from wurtzite. This species should therefore be classified as a sulfide. On the other hand, the minerals of tetrahedrite series, Cu$_{12}$(As,Sb)$_4$S$_{13}$, are often misconceived as derivatives of the sphalerite structure. However, arsenic and antimony in these minerals are trivalent and have the pyramidal coordination characteristics of sulfosalts. In fact, as pointed out by Wünsch (1964), the crystal structure of tetrahedrite cannot be derived directly from the sphalerite structure through the substitution of Zn by Cu and (As, Sb).

In the structure of a sulfosalts the presence of anionic groups, either single or polymerized, reminds us of the structure of a silicate in which SiO$_4$ tetrahedra play a similar role. However, there is a difference between these two structures; the interatomic bonds in the silicate are essentially ionic, while those in sulfosalts are covalent, which means that the former are non-directional and simple, while the latter are directional and a little more complex. Certainly due to this fact, the classification of sulfosalts on the basis of their structural principles has not been established. However, since a number of important members of this group, especially those containing Cu and Pb, have been investigated and their structures have been determined at least in their main features, it is believed that we should now direct our efforts to the problem of their classification.

In the present paper, we shall begin with a general survey of the dimensions of the TS$_3$ group and propose principles for classification. Then we shall describe their application to the structures of sulfosalts containing Pb as the major metal atom, and discuss general structural scheme of these sulfosalts based upon the dimensional relations between TS$_3$ pyramids and metal polyhedra.

**Dimensions of the TS$_3$ anionic groups**

A survey of bond lengths in the structures of sulfides in general was lately carried out by Berry (1965) and the bond lengths between trivalent atoms and sulfur atoms were also discussed. Since then, however, accurate structure determinations have been accomplished of some important members of sulfosalts, and more reliable data are now available. Therefore, it will be worthwhile revising and extending the survey. In the following, only those data from well-refined structures are employed, and bridge bonds of the S–T–S type and non-bridge
Structural principles and classification of sulfosalts

Table 1. As–S bond lengths in sulfosalts

<table>
<thead>
<tr>
<th>Bridge bond</th>
<th>Non-bridge bond</th>
<th>Bridge bond</th>
<th>Non-bridge bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>binnite¹</td>
<td>2.246 Å</td>
<td>marrite⁴</td>
<td>2.259 Å</td>
</tr>
<tr>
<td>hatchite²</td>
<td>2.35 Å</td>
<td>2.23</td>
<td>2.279</td>
</tr>
<tr>
<td></td>
<td>2.26</td>
<td>2.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.30</td>
<td>2.25</td>
<td></td>
</tr>
<tr>
<td>hutchinsonite³</td>
<td>2.31</td>
<td>2.30</td>
<td>2.304 Å</td>
</tr>
<tr>
<td></td>
<td>2.26</td>
<td>2.24</td>
<td>2.234</td>
</tr>
<tr>
<td></td>
<td>2.35</td>
<td>2.24</td>
<td>2.271</td>
</tr>
<tr>
<td></td>
<td>2.32</td>
<td>2.23</td>
<td>2.238</td>
</tr>
<tr>
<td></td>
<td>2.33</td>
<td>2.25</td>
<td>2.251</td>
</tr>
<tr>
<td></td>
<td>2.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.27*</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>wallisite⁷</td>
<td>2.31</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>2.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>xanthoconite⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td>2.31</td>
<td>2.26</td>
</tr>
</tbody>
</table>

* Bond lengths in the As–S sheet configuration of hutchinsonite.

¹ WUENSCH et al. (1966), ² MARUMO and NOWACKI (1967), ³ TAKÉUCHI et al. (1965), ⁴ WUENSCH and NOWACKI (1967), ⁵ ENGEL and NOWACKI (1966), ⁶ MARUMO and NOWACKI (1966), ⁷ TAKÉUCHI et al. (1968), ⁸ ENGEL and NOWACKI (1968).

Bond lengths between As and S are listed in Table 1. It will be noticed that bridge bonds are longer than non-bridge bonds. Some of the bridge bonds in hutchinsonite (TAKÉUCHI et al., 1965) are shorter than those of the rest in the table. In the structure of hutchinsonite some of the AsS₃ pyramids form a sheet by sharing every sulfur corner, and the shorter bonds are found in this sheet. The bridge bonds in orpiment, As₂S₃, whose structure is built up of a sheet of AsS₃ pyramids, also show similar values ranging from 2.21 Å to 2.28 Å (MORIMOTO, 1954), giving a mean value of 2.25 Å. Thus it seems certain that the bridge bonds in a sheet are shorter than the others, though the reason
Table 2. Sb—S bond lengths in sulfosalts

<table>
<thead>
<tr>
<th>Bridge bond</th>
<th>Non-bridge bond</th>
<th>Bridge bond</th>
<th>Non-bridge bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>berthierite</td>
<td>2.58 Å</td>
<td>2.48 Å</td>
<td>livingstonite</td>
</tr>
<tr>
<td></td>
<td>2.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.48</td>
<td>2.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>jamesonite</td>
<td>2.64</td>
<td>2.39</td>
<td>miargyrite</td>
</tr>
<tr>
<td></td>
<td>2.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.52</td>
<td>2.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.44</td>
<td>2.42</td>
<td>pyrargyrite</td>
</tr>
<tr>
<td></td>
<td>2.79</td>
<td></td>
<td>tetrahedrite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>mean</td>
</tr>
</tbody>
</table>

* Bond lengths were recalculated by the present authors.
** Bond lengths in the Sb—S sheet configuration of livingstonite.
1 BUERGER and HAHN (1955), 2 NIZZERI and BUERGER (1957b),
3 NIZZERI and BUERGER (1957a), 4 KNOWLES (1964),
5 ENGEL and NOWACKI (1966), 6 WUENCH (1964).

is unknown. On the other hand, CAMERMAN and TROTTER (1964) reported that the As$^{III}$—S single bond in cacodyl disulfide shows a length of 2.28 Å which falls between the mean value of bridge-bond lengths and that of non-bridge bonds in Table 1. However, the sulfur atom in this compound is bonded to one more arsenic atoms in the pentavalent state and accordingly forms a bridge bond, As$^{III}$—S—As$^{V}$. The deviation from our values may therefore be due to this particular situation.

Bonds between Sb and S given in Table 2 indicate a larger difference in length between bridge bonds and non-bridge bonds than for As—S bonds. As in the case of hutchinsonite, the bridge bonds in a sheet of linked Sb$_3$S in livingstonite (NIZZERI and BUERGER, 1957a) are shorter than the average.

The differences in length between bridge bonds and non-bridge bonds are still larger in sulfurbismuthites. The only well-refined structure
Table 3. Bi–S bond lengths in sulfosalts

<table>
<thead>
<tr>
<th>Bridge bond Non-bridge bond</th>
<th>Bridge bond Non-bridge bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>galenobismutite¹ 2.79 Å  2.63 Å</td>
<td>cosalite² 2.83 Å  2.62 Å</td>
</tr>
<tr>
<td>2.78</td>
<td>2.83</td>
</tr>
<tr>
<td>2.78</td>
<td>2.74</td>
</tr>
<tr>
<td>2.73</td>
<td>2.74</td>
</tr>
<tr>
<td>2.73</td>
<td>2.85</td>
</tr>
<tr>
<td>mean 2.77  2.63</td>
<td>mean 2.77  2.61</td>
</tr>
</tbody>
</table>

¹ Iitaka and Nowacki (1962), ² Weitz and Hellner (1960).

Table 4. Bond angles of TS₂ pyramids

<table>
<thead>
<tr>
<th>S–As–S</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>binnite</td>
<td>98°22'</td>
</tr>
<tr>
<td>hatchite</td>
<td>98°48' (mean)</td>
</tr>
<tr>
<td>hutchinsonite</td>
<td>98°12' (mean)</td>
</tr>
<tr>
<td>marrite</td>
<td>98°40' (mean)</td>
</tr>
<tr>
<td>proustite</td>
<td>99°24'</td>
</tr>
<tr>
<td>rathite I</td>
<td>98°00' (mean) A₈₁, A₈₂ and A₈₃</td>
</tr>
<tr>
<td>wallisite</td>
<td>98°36' (mean)</td>
</tr>
<tr>
<td>xanthoconite</td>
<td>99°12'</td>
</tr>
<tr>
<td>mean*</td>
<td>98°39'</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S–Sb–S</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>berthierite**</td>
<td>94°00' (mean)</td>
</tr>
<tr>
<td>livingstonite**</td>
<td>92°36' (mean)</td>
</tr>
<tr>
<td>miargyrite**</td>
<td>94°51' (mean)</td>
</tr>
<tr>
<td>pyrargyrite</td>
<td>96°20'</td>
</tr>
<tr>
<td>tetrahedrite</td>
<td>95°08'</td>
</tr>
<tr>
<td>mean</td>
<td>94°35'</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S–Bi–S</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>galenobismutite**</td>
<td>92°0' (mean) 81.7°, 93.4°, 95.0° and 97.3°</td>
</tr>
<tr>
<td>cosalite**</td>
<td>92°0' (mean)</td>
</tr>
</tbody>
</table>

* The average value of bond angles in nowackite (Marumo, 1967) is 101.63 ± 0.4° and it is certainly larger than others. Therefore, it was not used for calculating the mean value.

** Bond angles were calculated by the present authors.
of this group is galenobismutite (Iitaka and Nowacki, 1962), data for which are given in Table 3, together with those of the less refined structure of cosalite (Weitz and Hellner, 1960).

From the results of the above survey, we can conclude that for a certain kind of trivalent atom, the average length of bridge bonds is certainly greater than that of non-bridge bonds. Another conclusion to be drawn here is that the difference in length between bridge bonds and non-bridge bonds becomes larger with increasing atomic number of the trivalent atom, T. These facts are similar to those for the bonds

\[ \frac{\Delta l}{l} \]

in \((XO_4)^{n-}\) ions \((X = Si, P, S, Cl)\) as discussed by Cruickshank (1964). A quantity \(\Delta l\) can be defined as (length of bridge bond—length of non-bridge bond)/(length of non-bridge bond). The average value of \(\Delta l\) for each \(T-S\) \((T = As, Sb, Bi)\) was evaluated and plotted in Fig.1 together with that of each \(X-O\). As observed in this figure, \(\Delta l\) of the \(T-S\) bonds shows a linear variation with atomic number similar to that of \((XO_4)^{n-}\) ions.

\(^2\) Calculated from the data appearing in Cruickshank (1964).
Because of the $p$-orbital nature of the bonds in $TS_3$ groups, the bond angles are expected to approach $90^\circ$ as the bond lengths between $T$ and $S$ increase. As seen in Table 4, this relation does hold for the $TS_3$ groups. Thus, as reasonable measures for dimensions of the $TS_3$ groups, the following values may be proposed:

<table>
<thead>
<tr>
<th>Bond type</th>
<th>$AsS_3$</th>
<th>$SbS_3$</th>
<th>$BiS_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length</td>
<td>bridge</td>
<td>2.31 Å</td>
<td>2.54 Å</td>
</tr>
<tr>
<td></td>
<td>non-bridge</td>
<td>2.26 Å</td>
<td>2.46 Å</td>
</tr>
<tr>
<td>Bond angle</td>
<td>98.8°</td>
<td>94.6°</td>
<td>92.0°</td>
</tr>
</tbody>
</table>

Next, we shall refer to $S$—$S$ edge lengths in the $TS_3$ groups where we must take possible deformation of bond angles into account. If two pyramids share an edge, the bond angles concerned will become smaller, while if a pyramid shares an edge with a coordination polyhedron (around lead for example) the bond angle concerned will become larger. After due consideration has been paid to these circumstances, the $S$—$S$ edge lengths are estimated to fall in the ranges: $3.4$—$3.6$ Å for $AsS_3$, $3.6$—$3.8$ Å for $SbS_3$, and $3.8$—$4.1$ Å for $BiS_3$.

So far we have taken into account the three shortest distances between $T$ and $S$ in the $TS_3$ group with the assumption that the bonds involved are solely of $p$-orbital character. However, the facts revealed by the crystal structure of stibnite, $Sb_2S_3$, should also be considered. According to Ščavnčar (1960), the structure contains a ribbon-like configuration with the composition $Sb_2S_6$. Two kinds of $Sb$ atoms, $Sb(1)$ and $Sb(2)$, exist in a ribbon. $Sb(1)$ is surrounded by three sulfur atoms and $Sb(2)$ by five. Therefore, the bonds for $Sb(1)$ are presumably of $p$ character, the $S$—$S$ distances being $2.58$ Å for bridge bonds and $2.57$ Å for non-bridge ones and the mean bond angle, $91.43^\circ$. For $Sb(2)$, Ščavnčar assumed octahedral $sp^3d^2$ orbitals in which a pair of electrons forms a lone pair. The five sulfur atoms thus constitute a square pyramid with an antimony atom situated roughly at the centre of the basal square. The distances from $Sb(2)$ to two basal sulfur atoms are $2.68$ Å; to the other two basal atoms $2.82$ Å; and to the apical atom $2.49$ Å; and the mean bond angle is $89.19^\circ$. This fact suggests that some of the $T$—$S$ bonds in sulfosalts may also be of octahedral character. As a matter of fact, five coordination around antimony can be noticed in the structure of berthierite, $FeSb_2S_4$ (Buerger and Hahn, 1955) and livingstonite, $HgSb_4S_8$ (Nizeki and Buerger, 1957a), though three sulfur atoms of the five are appreciably nearer to anti-
mony than those in the case of stibnite. If the octahedral orbitals are involved in T—S bonds, the T atom is expected to be surrounded by seven sulfur atoms as shown in Fig. 2, because repulsion arises between the lone-pair electrons and the sulfur atoms, and in fact, those antimony atoms in stibnite, berthierite and livingstonite have seven neighbouring sulfur atoms.

![Fig. 2. Octahedral neighbours of a TS<sub>3</sub> group which utilizes ρ<sup>3</sup> orbitals (left), and seven neighbours of sulfur atoms around a T atom which utilizes sp<sup>3</sup>d<sup>2</sup> orbitals (right). The lower figures indicate the projections of each polygon along its vertical edges.](image)

On the other hand, in addition to ρ<sup>3</sup> orbitals, tetrahedral sp<sup>3</sup> orbitals are also possible in certain sulfosalts. The bond angles of SbS<sub>3</sub> pyramids in chalcostibite, CuSbS<sub>2</sub> (Hoffmann, 1933), suggest that the bonds are of tetrahedral character, where a pair of electrons forms a lone pair.

**Classification of sulfosalts**

In order to classify the sulfosalts, we must first establish what principles govern the general relationship between the chemical compositions and the crystal structures of this group of minerals. As far as our survey of all the refined structures is concerned, we believe that the principle determining the structure is the dimensional relationship between the coordination polyhedra around monovalent and divalent metal atoms which we shall call ‘A atoms’ hereafter, and those around trivalent atoms which we shall call ‘T atoms’. Accordingly, the radii of
these constituent atoms can be considered as effective parameters for the classification. This will be exemplified in the subsequent section on the structures of the Pb-bearing members.

On the other hand, however, the radii of these atoms for various coordination states cannot unambiguously be determined. Therefore, we here propose as tentative measures of their atomic sizes the principal quantum numbers of the valence shells of these atoms.

Since there are a number of sulfosalts which contain two, or more than two, kinds of A atoms, we introduce the ‘average principal quantum number’, \( \bar{n}(A) \), defined as

\[
\bar{n}(A) = \frac{\sum k_i \cdot n(A_i)}{\sum k_i},
\]

where \( n(A_i) \) is the principal quantum number for the valence shell of an A atom of the kind \( i \), and \( k_i \) is the number of the atoms per formula unit. The quantity, \( \bar{n}(A) \), will thus be a measure of the average size of A atoms existing in a structure. This parameter will also be used as a measure of the directional character of metal atoms involved in a structure (Pearson, 1964).

Next, we take a ratio, \( \frac{\sum n(A_i)}{\sum n(T_j)} \), where \( n(T_j) \) indicates the principal quantum number for the valence shell of a T atom of the kind \( j \), and summations should be made for the formula unit. This ratio is intended to serve as an indication of the volume occupied by A atoms relative to that occupied by T atoms in the structure under consideration. A diagram of \( \bar{n}(A) \) vs. \( \frac{\sum n(A_i)}{\sum n(T_j)} \) was then prepared and the natural crystalline phases of sulfosalts were plotted (Fig. 3). As will be observed, this diagram is roughly divided into four parts according to the structural characteristics of the crystalline phases.

Area I covers the sulfosalts which contain copper as a major component. The crystal structures of sulfosalts which fall in this area are thus characterized by the linkages of Cu tetrahedra (e.g. tetrahedrite) or those of Cu tetrahedra and TS₂ pyramids (e.g. chalcostibite). At the right of this area, there is located a group of sulfosalts—seligmannite, PbCuAsS₃; bournonite, PbCuSbS₃, and aikinite, PbCuBiS₃. Hellner and Leineweber (1956) showed that they have similar structures and pointed out the similarity between their structures and that of stibnite. However, Takeuchi and Haga (1969) refined the atomic parameters of seligmannite using the structure amplitudes given by Leineweber (1956), and proposed a new view that it is essentially built up of a three-dimensional framework consisting of CuS₄ tetrahedra and AsS₃.
Fig. 3. The relations between the chemical compositions and the crystal structures of sulfosalts. Representative minerals in each area are:

Area I
1. binnite, (Cu,Fe)$_2$As$_2$S$_6$
2. tetrahedrite, (Cu,Fe)$_2$Sb$_2$S$_6$
3. chalcocite, CuSbS$_2$
4. emplisite, CuBiS$_2$
5. berthelite, Pb$_2$CuSb$_2$S$_6$
6. seligmannite, Pb$_3$Al$_2$Sb$_2$S$_6$
7. bournonite, Pb$_3$SbS$_3$
8. aikinite, PbCuBiS$_2$

Area II
1. polyargyrite, Ag$_5$Sb$_2$S$_6$
2. pearceite, (Ag,Cu)$_{14}$As$_6$S$_{11}$
3. polybasite, (Ag,Cu)$_{14}$Sb$_{11}$S$_{11}$
4. stephanite, Ag$_8$Sb$_8$
5. xanthoconite, Ag$_2$As$_2$
6. pyrargyrite, Ag$_5$Sb$_2$S$_6$

Area III
1. lengenbachite, Pb$_3$Ag$_6$Cu$_{18}$As$_{28}$S$_{79}$
2. gratonite, Pb$_3$As$_4$S$_{13}$

Area IV
1. geocronite, Pb$_3$(Sb,As)$_2$S$_8$
2. beegerite, Pb$_3$Bi$_3$S$_9$
3. jordane, Pb$_3$As$_4$S$_8$
4. menophinite, Pb$_3$CuSb$_2$S$_8$
5. hatchite, TIPbAgAs$_3$S$_4$
6. freieslebenite, Pb$_3$AgSb$_3$S$_8$
7. wallisite, TIPbCuAs$_3$S$_4$
8. diaphorite, Pb$_3$Ag$_2$Sb$_3$S$_8$
9. smithite, AgAs$_2$
10. smithite, Pb$_3$As$_2$

Details of the mineral species on the vertical axis of $\bar{n}(A) = 6$ in the area IV are described in Fig. 7.
pyramids, lead atoms being inserted in the large spaces in the framework. In general, in the crystal structures of sulfosalts of this area the linkages of Cu tetrahedra, or those of Cu tetrahedra and TS₂ pyramids, are closely related to the simple tetrahedral structures observed in sulfides.

Area II covers the silver sulfosalts containing more silver. Although only the crystal structures of pyrargyrite, Ag₃SbS₉ (Harker, 1936; Engel and Nowacki, 1966), and xanthoconite, Ag₃AsS₉ (Engel and Nowacki, 1968), are known, the crystal structures of these sulfosalts are characterized by covalent bonds which are specific to the silver atoms.

The minerals which fall in the area III, which extends from the central part to the diagram upper to the right, are indicated by solid hexagons. Most of these sulfosalts were investigated by x-ray methods and it has been found that their structures are closely related to the galena-type structure. Matildite, Ag₃BiS₉ (Geller and Wernick, 1959), miargyrite, Ag₃SbS₉ (Knowles, 1964), freieslebenite, PbAgSbS₉ (Hellner, 1957) and diaphorite, Pb₂Ag₃Sb₂S₉ (Hellner, 1958) are typical examples. They all are based upon the PbS-type structure, and in fact
they transform to disordered PbS-type structures at an elevated temperature (Wernick, 1960). Although in the crystal structure of wallisite (Takéuchi et al., 1968), which contains copper as a major component, the copper tetrahedra and AsS₃ pyramids form a composite chain, the arrangements of lead and sulfur atoms are closely related to the galena structure. Some other minerals in this area, like lennangachite, Pb₃₈Ag₇Cu₆As₂₈S₇₈, and franckeite, Pb₂Sn₂Sb₂S₁₄, give diffraction patterns which are characterized by a marked subcell of the galena type (Fig. 4), suggesting that, in spite of the complexity of the chemical compositions, the structures are based upon that of galena.

The final area IV, which extends from the lower right part of the diagram to the left, covers the great majority of the lead sulfosalts. Since these are relatively rich in trivalent atoms, they show, in contrast to the singular aspect common to the lead sulfosalts in the area III, various structures depending upon the Pb-to-T atom ratio. If the ratio is higher, the structures are characterized by the linkage of lead polyhedra while, if the ratio is lower, they are characterized by those of the pyramids of T atoms. Therefore their structures are primarily to be interpreted in terms of the dimensional differences between lead polyhedra and T pyramids. Thus, from the structural view point, they are the most interesting subgroup of sulfosalts, and the variation of their structures with chemical compositions is discussed below, in terms of the above-mentioned dimensional differences.

With this diagram (Fig. 3) the basic principles of the crystal structure of a given sulfosalts could be predicted, provided that its chemical composition were known. However, this diagram seems to be less applicable to sulfosalts which contain transitional elements as metal atoms. For instance, samsonite, MnAg₂Sb₂S₆ for which $\bar{n}(A) = 4.8$, $\Sigma n(A) \Sigma n(T) = 2.4$, falls in the area I, but it is not likely that the structure is characterized by a tetrahedral linkage of metal atoms.

**General characteristics of lead sulfosalts**

The most common coordination of lead in sulfides is octahedral, as occurs in galena, the Pb–S distance being 2.965 Å (Swanson and Fuyat, 1953). This bond length in galena implies that the edges of the octahedra are 4.19 Å long, provided that the octahedra are of regular shape. This value is longer than the edges in any TS₃ pyramids. Therefore sharing edges between octahedra and pyramids inevitably gives rise to a deformation of these polyhedra. Since bonds in pyramids are stronger than those in octahedra, it is expected that the deformations
are much more conspicuous for octahedra. Greater deformations are evidently to be expected if the lead octahedra share edges with As$_3$ pyramids, the smallest. For this case, as shown in Fig. 5, the deformations in octahedra produce a fairly large open space which allows further sulfur atoms to approach the central lead atom, thus increasing

![Diagram](image1)

**Fig. 5.** Deformations of a Pb-S octahedron caused by sharing an edge with an Sb$_3$ pyramid (left), and with an As$_3$ pyramid (right)

![Diagram](image2)

**Fig. 6.** A regular Pb-S octahedron (a) may be deformed (b) if it shares an edge with a certain TS$_3$ group, producing an open space which allows further sulfur atoms to approach the lead atom. If one sulfur atom approaches, a lead polyhedron of coordination number seven results (c); if two approach, that of coordination number eight is obtained (d). Further deformations of the Pb-S polyhedron by sharing edges with TS$_3$ groups finally yield the polyhedron of nine-fold coordination (e)
the coordination of lead. In fact, in most of the lead sulfarsenites, lead atoms have coordination number nine, which is the highest so far observed for lead. Six of the nine sulfur atoms in such lead polyhedra form, as illustrated in Fig. 6, a trigonal prism whose edges are of lengths similar to those in lead octahedra and each of the other three sulfur atoms forms a square pyramid on each prism face.

Since SbS$_3$ and BiS$_3$ pyramids cause relatively less distortion of lead octahedra, the lead polyhedra in the structure of sulfantimonites and sulfbismuthites generally take a form intermediate between octahedra and the nine-coordinated polyhedra just mentioned. They may also be distorted octahedra (Fig. 6). The coordination number of lead in these sulfosalts is therefore 6, 7, 8. The ratio between the number of octahedra and the number of intermediate polyhedra in a structure depends on the content of lead relative to that of the $T$ atoms.

These relations among the lead sulfosalts can be systematized if we apply the principle discussed in the preceding section. Using it, we can further classify the lead sulfosalts. We then introduce two parameters: the first is the principal quantum number of the trivalent atoms, $n(T)$, and the other is $\Sigma n(A_0)/\Sigma n(T_j)$ just as the diagram of Fig. 3. Figure 7 is then a diagram in which the second parameter is plotted along the vertical axis and the first along the horizontal. On the left of this diagram there appear only sulfarsenites, in the middle sulfantimonites and on the right sulfbismuthites. The area of this diagram can be roughly divided into three parts according to types of lead polyhedra occurring in the structures.

In the structures of sulfosalts in the upper right area of this diagram, both octahedra and intermediate polyhedra occur, and in those of the central area, only intermediate types. In those of the left part, which covers the sulfarsenites, the nine-fold coordination appears. Among sulfarsenites, hutchinsonite (Takéuchi et al., 1965) which is most rich in arsenic, is somewhat exceptional. Since half of the arsenic atoms of hutchinsonite form a sheet structure, the number of arsenic atoms surrounding lead-sulfur polyhedra is less than in other sulfarsenites. Thus only intermediate polyhedra of lead occur in its structure. With this exception of hutchinsonite, we can observe that, in this diagram, the coordination number of lead increases from the upper right to the lower left.

Such a general tendency in the structures of lead sulfosalts can be explained as follows: As already discussed, bismuth and antimony may have coordination polyhedra which simulate distorted octahedra,
though bonding is only with the three closest neighbors. These distorted octahedra tend to form, together with lead octahedra, a fragment of the galena-type structure. If the ratio of $\sum n(A)$ to $\sum n(T)$ is

Fig. 7. Relations between chemical compositions and types of lead polyhedra of sulfosalts in the area IV (Fig. 3). Representative minerals are explained below. Since each chemical formula has a general form, $Pb_mT_nS_p$, it is given in an abbreviated form, $mnp$. Those which have not the general form are given in full.

Area A
1 lillianite*, 3 2 6
2 cosalite, 2 2 5
3 kobellite*, 2 2 5
4 semayite*, 9 8 21
5 boulangerite, 2 2 5
6 heteromorphite*, 7 8 19

Area B
1 veenite*, 2 2 5
2 fizolyite**
3 jamesonite**
4 andorite**
5 plagonite*, 5 8 17
6 zinkenite, 6 14 27
7 fuloppite*, 3 8 15

Area C
1 dufrenoisite, 4 4 10
2 rathite-Ia, 7 9 20
3 rathite-II, 9 13 28
4 rathite-I, 3 5 10
5 baumhauerite, 5 9 18
6 scleroclase, 2 4 8

Area D
1 hutchinsonite, $PbTIAs_3S_8$

* Unknown structure.

** Chemical formula is given in Fig. 3.
large, the distortions in the fragments may be accommodated locally and the whole structure is of the galena type. On the other hand, if the ratio becomes smaller, the distortions in fragments increase and the extent of the fragments is limited. Therefore, they join in various ways to form a structure. In the boundaries between these fragments, the intermediate type of lead polyhedra occurs (Fig. 8). The occurrence of these intermediate polyhedra (which are not octahedra) presumably plays a role in minimizing the distortions accumulated when the fragments are joined. This is the case of sulfosalts in the upper right area of the diagram. Now, as the ratio decreases further, the fragments come to consist solely of trivalent atoms, and the lead atoms occur only in the boundaries of these fragments. This is the case of sulfosalts in the central area of the diagram. Since the pyramids of arsenic atoms have the smallest dimensions, they no longer form structural fragments of the galena type in the structures of sulfarsenites of the left part of the diagram, and lead octahedra are generally highly deformed to have the nine-fold coordination.

Fig. 8. The crystal structure of cosalite projected along the $c$ axis, showing the fragments of the galena-type structure (shaded area). The bonds of intermediate Pb-S polyhedra are indicated by heavy lines. Large circles are sulfur atoms, and small ones in the shaded area are lead or bismuth. The shaded circles and open circles are respectively at $z = 3/4$ and $z = 1/4$ [after Weitz and Hellner (1960), but with some changes]
Next, we discuss in a different way the effects of the dimensional differences between pyramids and lead polyhedra. In the structure of lead sulfosalts, the nine-coordinated polyhedra tend to share basal triangles to form an infinite chain, while octahedra share edges and also form an infinite chain (Fig. 9). Since both chains have repeat distances of about 4.19 Å, the great majority of lead sulfosalts have cell edges of about 4.19 Å or its multiples. Without exception the single repeat distance appears in sulfbismuthites. This is because the BiS$_3$ pyramids are the largest and their edge lengths are very close to those of lead octahedra. Therefore BiS$_3$ pyramids may share corners and form an infinite chain whose repeat distance is in conformity with that of lead chain. Figure 10 shows the general scheme of how the lead chains and BiS$_3$ chains are connected together. It should be noted that, in sulfbismuthites, the repeat distances along the chain directions are around 4.10 Å and less than the ideal repeat distance of the lead chains. Therefore, the slightly smaller repeat distance of the BiS$_3$ chains presumably causes the shrinkage of lead chains along their lengths.

On the contrary, the single repeat distance never occurs in sulf-arsenites but the repeat distances are generally multiple of just about 4.19 Å, the ideal value. This is explicable in that the edges of AsS$_3$
pyramids are much smaller than those of the lead polyhedra and, thus, for this case of sulfarsenites the formation of infinite chains like BiS$_3$ is not possible but the AsS$_3$ pyramids form various finite chains along the chain direction of lead polyhedra as given in Fig. 11. The arrangement of these finite chains along lead chains determines the repeat distance of a structure along the direction of the lead chains, and therefore, the single repeat distance of the lead chains is no longer the true repeat distance in this direction. Since it is conceivable that such a mode of arrangement of finite chains minimizes the deformation of lead chains along their lengths, the repeat distance of lead chains may retain their ideal value 4.19 Å. In this way, it is understandable why the repeat distances of sulfarsenites along the chain direction are multiples of the ideal 4.19 Å. The repeat distances or sub-repeat distances along chain directions are compared for sulfbismuthites, sulfantimonites and sulfarsenites in Fig. 12.

The dimensions of SbS$_3$ pyramids are in between those found in the above two cases and, as observed in Fig. 12, the repeat distances along lead chains do not show a characteristic value as do other cases, but are distributed over a wide range. We can observe, in fact, various types of SbS$_3$ linkages in sulfantimonites. They may be divided into three categories. Firstly, along lead chains SbS$_3$ pyramids form single infinite

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![Diagram](image-url)
chains like BiS$_3$. Such a configuration of pyramids appears especially in the structures which contain smaller metal atoms like Fe in addition to lead. Thus this type of chain is observed in berthierite, FeSb$_2$S$_4$ (Buerg er and Hahn, 1955), and jamesonite, FePb$_2$Sb$_6$S$_4$ (Nizeki and Buerg er, 1957$b$). For these cases, if lead is present, the Pb-S chain is subject to contraction along the chain direction and shows a smaller repeat distance than 4.19 Å. For example, the repeat distance of jamesonite along chain direction is 4.03 Å. Secondarily, the pyramids form a complex chain so as to minimize the deformation of Pb-S chains. An example of such a chain has been reported for livingstonite,
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HgSb₄S₈ (Niseki and Buerger, 1957a). Finally, the pyramids form a lateral linkage with respect to lead chains, as two of the three non-equivalent Sb in jamesonite (Fig. 13). These various possible linkages of Sb₄S₈ pyramids may account for the various repeat distances of sulfantimonites along lead chains.

In addition to the lead sulfosalts so far discussed, there are, in area IV of the diagram (Fig. 3), a few sulfosalts which contain thallium atoms as A atoms like lorandite, TlAsS₃, and rvaite, TlAs₂SbS₅. However, owing to the fact that thallium atoms tend to form a polyhedron of sulfur atoms which is different from lead-sulfur polyhedra as observed in lorandite (Zemann and Zemann, 1959), a slight modification of the above discussions would be necessary to extend them to the sulfosalts whose A atoms are solely thallium.

The authors wish to thank Dr. A. L. Mackay for discussions and reading manuscript, and Dr. M. Ohmasa for his assistance in computations.

Added in proof: After this paper was sent for publication, Professor Menzer kindly pointed out us a Nowacki's paper presented at the meeting of crystallographers at Bern, October 1968, whose abstract was later published in this journal, Vol. 128 (1969) 427-428 and full paper in Schweizer Mineralogisch-Petrographische Mitteilungen, Vol. 49 (1969) 109-156 under the title "Zur Klassifikation und Kristallchemie der Sulfosalze". In this paper, Nowacki mainly discussed the configurations of anionic groups consisting of T₅S₈ pyramids in terms of \( \varphi \) value, the ratio of the number of S atoms to that of T atoms in a formula unit. He then showed that possible topological features of the anionic groups are deduced from a given \( \varphi \) value.

In connection with our paper, we should also mention a work done by E. Hellner [A structural scheme for sulfide minerals. J. Geol. 66 (1958) 503-525], in which he successfully systematized the structures of sulfides and sulfosalts on the basis of the closest-packings of sulfur atoms. After his work was published, a number of detailed structures have become available, giving an information on the distortions of sulfur lattices mainly due to the formation of T₅S₈ pyramids characteristic of sulfosalts. Since distortion of a structure is an important aspect in crystal chemistry, we placed much stress upon this point.

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