Zeitschrift:	Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie
Band:	67 (1987)
Heft:	3
Artikel:	TI+, Pb2+, and Bi3+ bonding and ordening in sulfides and sulfosalts
Autor:	Hummel, Wolfgang / Armbruster, Thomas
DOI:	https://doi.org/10.5169/seals-51599

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. <u>Mehr erfahren</u>

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. <u>En savoir plus</u>

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. <u>Find out more</u>

Download PDF: 17.08.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

Tl⁺, Pb²⁺, and Bi³⁺ bonding and ordering in sulfides and sulfosalts*

by Wolfgang Hummel¹ and Thomas Armbruster¹

Abstract

The inorganic crystal structure database (ICSD) was employed to study Tl, Pb, and Bi bonding and ordering relations in sulfosalts. A bond valence model with one common parameter for Tl, Pb, and Bi is successfully used to separate these elements on the basis of their Me-S distances. Application of this concept on (Tl,Pb)-bearing sulfosalts indicates preferred Tl,Pb ordering, in contrast to (Bi,Pb)-bearing sulfosalts, where Pb,Bi order and disorder is observed. Isotropic displacement equivalents (B_{eq} values), compiled from the data base, yield mean values of 2.8 for Tl⁺, 2.3 for Pb²⁺, and 1.4 for Bi³⁺. The differences in mean B_{eq} values are discussed in terms of increasing Me-S bond strengths from Tl⁺ to Bi³⁺.

Keywords: Sulfosalts, Lengenbach, Crystal structure database, isoelectronic series, displacement parameters.

Introduction

Sulfosalt structures may simultaneously contain Bi³⁺, Pb²⁺, and Tl⁺ or combinations of two of these elements, which cannot be distinguished by their scattering behavior of X-rays because they are isoelectronic (80 electrons). In addition, the application of mean Me(Tl,Pb,Bi)-S bond lengths is restricted because MeS_x coordination polyhedra are often strongly distorted due to the influence of the lone electron pair. In a previous study (ARM-BRUSTER and HUMMEL, 1987) a simple diagram was developed where the mean value of the three shortest Me-S distances is plotted versus the mean value of the next two shortest ones. This diagram was successfully applied to distinguish Bi and Pb in sulfosalts.

In the present study special emphasis is put on bonding and ordering of Pb and Tl. Crystal structure data of sulfides and sulfosalts are statistically analyzed using the above distance scheme and the bond valence approach recently reviewed by BROWN and ALTERMATT (1985). In addition, the isotropic displacement parameters (temperature factors: B_{eq} of B) will be compared for the isoelectronic series: Tl⁺, Pb²⁺, and Bi³⁺.

Experimental

All structural data analyzed were extracted from the inorganic crystal structure database, version 1986 (ICSD) (BERGERHOFF et al., 1983). For construction of reference diagrams only following structures were considered:

(a) Crystal structures at room temperature with sulfur and Tl or Pb or Bi but not with combinations of Bi, Pb, Tl or any two of these elements. (b) Structures containing oxygen (SO_4^{2-}) , carbon (SCN-), nitrogen, selenium, tellurium or halogen were excluded.

^{*} Dedicated to the "Arbeitsgemeinschaft Lengenbach" for 30 years of continuous cooperation on sulfosalt research.

¹Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestr. 3, CH-3012 Bern.

(c) Structures with R-values > 9% or without R-values were excluded.

(d) Tl, Pb, Bi positions with mixed or partial occupancy < 90% were excluded.

The resulting database contained 40 Tl, 25 Pb, and 14 Bi sulfosalt- or sulfide-structures (Table 1). To exclude errors either in the data base or in the original literature, the bond valence model of BROWN and ALTERMATT (1985) was applied:

$$V = \Sigma S_{ij} = \Sigma \exp((\frac{r_o - r_{ij}}{0.37})),$$

where r_{ij} are the individual Me–S distances. Me–S distances < 3.8 Å for Tl, < 3.6 Å for Pb, and < 3.5 Å for Bi were calculated. For all bond valence calculations a fixed r_0 parameter of 2.543 was employed, independently of whether Tl⁺, Pb²⁺, or Bi³⁺ was studied.

Atomic positions yielding valence sums (V) outside the range 0.7-1.3 (Tl), 1.7-2.3 (Pb), and 2.7-3.3 (Bi) were checked with the original reference and, if necessary, deleted or corrected*. The final database contained 84 Tl positions,

70 Pb positions, and 30 Bi positions. If displacement parameters for Tl⁺, Pb²⁺, and Bi³⁺, either as β_{ij} , U_{ij}, B_{ij} or as isotropic B or U, were given in ICSD (Table 1), the displacement parameters were transformed into B_{eq} (HAMIL-TON, 1959) or B values. At this instance additional obvious errors were detected in ICSD which were corrected in our files by comparison with the original literature*.

Results

The final bond distance diagram and bond valence histogram are displayed in Fig. 1 and 2a, respectively. Both models yield trimodal distributions which can be applied to distinguish Tl, Pb, and Bi in sulfosalts. Surprisingly, the bond valence diagram (Fig. 2a) separates the isoelectronic elements even better than the bond distance plot (Fig. 1) proposed by ARM-BRUSTER and HUMMEL (1987).

* All errors detected in ICSD were reported to the ICSD senior author Bergerhoff for subsequent correction.

Tl	Tl	Pb	Pb	Bi	Т1.РЪ	Pb.B
					/	
640	36368	67	36348*	1132*	14112	167
1911	36369	2221	36473	1942	26785	2737
2240	38255	2222	38293*	2839	26804	9120
2647	38363	2439	100688*	14305	27304	14245
14187	48133	8166	200601	15230	27481	15229
15231	49542	8167		23315	31364	23905
15240	49681	8168		23663	100315	24462
15494	61057	14303		30775		30776
17035	100161	14304		32585	10 10	30780
17058	100291	15143		34936		31382
17065	100292	16272		38364		35596
23290	100374	16317		47131		60156
23634*	100438	16978		200794		60159
25354*	100849	18097		201066		100335
25355*	201026	18123				200113
31358	201062	23264			8	
32607	201422	23462				
33531	201423	23661	4			
35041	201889	27183			2	
35498	201892	31254*				

Tab. 1	Collection codes of selected sulfides and sulfosalts in ICSD	BERGERHOFF et al	1983)
			,

* no temperature parameters in ICSD

Note: References corresponding to collection codes may be obtained from the authors.

In addition, some peculiar observations were made during the compilation of the reference diagrams. Tl³⁺ is reported in the structure of Tl₄S₃ (LECLERC and BAILLY, 1973), where Tl³⁺ exhibits tetrahedral coordination by S with TI-S distances ranging between 2.51 and 2.59 Å. Strongly distorted 4-fold coordinated Tl+ is observed in TlMnAS₂S₅ (Gostonic et al., 1982), $Tl_2Sn_2S_3$ (DEL BUCCHIA et al., 1982), and Tl₄SnS₃ (DEL BUCCHIA et al., 1981) with Tl-S distances between 2.8 and 3.5 Å. In wittichenite, Cu₃BiS₃, (KOCMAN and NUFFIELD, 1973) a BiS₃ trigonal pyramid exhibits three short Bi-S distances (2.569, 2.600, 2.608 Å) and additional long ones. Because a cutoff value of 3.5 Å was chosen for Bi-S distances, only one additional distance at 3.43 Å was considered in our compilations. Coordination numbers < 5 are not included in Fig. 1, but corresponding coordinations are marked by open symbols in Fig. 2a. During the compilation of distances it was observed that in several cases Me-As or even Me-Me distances were shorter than some long Me-S distances. However, the sums of bond



Fig. 1 The mean value of the three shortest Me-S distances is plotted versus the mean value of the next two shortest ones. All data are obtained from published structures (Table 1). For selection criteria see text. Dotted lines confine various distribution clouds which are slightly different to the ones outlined by ARMBRUSTER and HUMMEL (1987) because in this paper a much larger number of Tl structures was included. The solid line indicates undistorted coordination where (D1+D2+D3)/3 = (D4+D5)/2.

valences yielded reasonable values even if neglecting additional Me-As or Me-Me interactions.

Applying the Me-S distance limits given above, following average coordination numbers of Me by sulfur were observed (standard deviations in parentheses), Tl⁺: 6.8(1.5), Pb²⁺: 7.7(1.0), Bi³⁺: 6.3(1.0). The coordination num-



Fig. 2a Histogram of calculated valence sums (V) for Tl, Pb, and Bi. Me-S distances were used to calculate valence sums for Me positions according to the empirical bond strength model proposed by BROWN and ALTERMATT (1985) with a common parameter for Tl⁺, Pb²⁺, and Bi³⁺. Open symbols indicate 4-coordinated positions. No overlap between Tl, Pb, and Bi is observed. Thus, the diagram can be used to distinguish these cations in sulfosalt structures.



Fig. 2b Data from (Tl,Pb)-bearing structures (black bars) and of (Pb,Bi)-bearing structures (open bars) are plotted according to Fig. 2a. (Pb,Bi)-bearing sulfosalts show ordered and disordered Pb,Bi distributions, whereas only Pb,Tl ordering is observed for (Pb,Tl)-sulfosalts (Table 2).



Fig. 3 The mean value of the three shortest Me-S distances of (Pb,Tl)-bearing sulfosalts is plotted versus the mean value of the next two shortest Me-S distances. Dotted and solid lines were adopted from Fig. 1. The striking separation of the data into two groups, one in the Tl field and the other in the Pb field, indicates preferred Pb,Tl ordering.

ber of Bi^{3+} by S ranges between 4 and 8, of Pb^{2+} between 6 and 9, and the one of Tl^+ between 4 and 10.

(Pb,Tl)-BEARING SULFOSALTS

The inorganic structure database contains seven sulfosalts with Tl and Pb in significant concentrations (Table 2). Two are synthetic, four originate from the Lengenbach sulfosalt quarry in the Binna valley (Wallis, Switzerland), and one sample comes from Jas Roux

(France). The observed (Pb,Tl)-S distances were plotted in the distance reference diagram (Fig. 3) also showing the characteristic fields for TI-S and Pb-S bonds, as derived from Fig. 1. The calculated valences, using the above formula by BROWN and ALTERMATT (1985), for (Pb,Tl) sulfosalts are plotted in Fig. 2b. Both diagrams (Fig. 2b and Fig. 3) indicate that all structures analyzed show preferred Tl and Pb For rathite-I (MARUMO ordering. and NOWACKI, 1965) no precise microprobe analyses are given for the sample used for structure refinement. Thus, according to our diagrams it seems probable that the rathite-I investigated contains only very low Tl concentrations. Other rathites-I, analyzed by NOWACKI and BAHEZRE (1963), yielded T1/ (T1+Pb) ratios of about 0.1. In contrast to the preferred ordering between Pb²⁺ and Tl⁺, Pb²⁺ and Bi³⁺ exhibit also disordered arrangements as discussed by ARMBRUSTER and HUMMEL (1987) and displayed according to the valence method in Fig. 2b.

DISPLACEMENT PARAMETERS OF Tl⁺, Pb²⁺, AND Bi³⁺

In the previous section, order/disorder relations between different ions on different structural positions were discussed, whereas this section refers to order/disorder relations of one ion about one "average position". The displacement parameters (B_{eq} or B) in the isoelectronic series: Tl⁺, Pb²⁺, Bi³⁺ should reflect the static and/or dynamic disorder of the metal within its distorted S coordination.

The reader is reminded that Tl^+ , Pb^{2+} , and Bi^{3+} belong to the heaviest stable isotopes

Composition	mineral name (origin)	Reference
$(T1,Pb)_2As_5S_9$	hutchinsonite (Lengenbach)	Takéuchi et al. (1965)
$(Pb,Tl)_3As_4(As,Ag)S_{10}$	rathite-I (Lengenbach)	Marumo and Nowacki (1965)
PbTlAgAs ₂ S ₅	hatchite (Lengenbach)	Marumo and Nowacki (1967)
PbTlCuAs ₂ S ₅	wallisite (Lengenbach)	Takéuchi et al. (1968)
$\mathrm{Tl}_8\mathrm{Pb}_4\mathrm{Sb}_{21}\mathrm{As}_{19}\mathrm{S}_{68}$	unnamed (Jas Roux)	Nagl (1979)
Tl ₂ PbGeS ₄	synthetic	Eulenberger (1980)
PbTlAs ₃ S ₆	synthetic	Balić-Žunić and Engel (1983)

Tab. 2 (Pb,Tl) containing sulfosalts.

within the periodic table. Thus, especially experimental neglects in X-ray intensity collection or data handling systematically influence the displacement parameters: insufficient absorption and/or extinction correction, neglect of anomalous dispersion effects etc. Fig. 4 shows a plot of Me valences, according to the bond strength concept, versus isotropic displacement parameters (Beq or B). Despite their strong dependence from experimental procedures, mean B_{eq} values calculated without the outlying points (open symbols in Fig. 4) for Tl+, Pb²⁺, and Bi³⁺ yield 2.8(5) for Tl⁺, 2.3(6) for Pb2+, and 1.4(3) for Bi3+ (standard deviations in parentheses). The stronger the interaction or bonding between Me(Tl⁺, Pb²⁺, Bi³⁺) and coordinating S, the weaker the dynamic Me disorder (thermal motion); thus, leading to displacement parameters which are the highest ones for Tl⁺ and lowest ones for Bi³⁺ (provided that the B_{eq} values are not dominated by effects related to static [positional] disorder).

Some outlying points (open symbols in Fig. 4) can be discussed on the basis of special structural features. The Tl positions in the layer-structure of TlInSiS₄ (NAKAMURA et al., 1984) with B_{eq} values of 6.6 and 7.3, respectively, are located between two sheet units with Tl-S distances between 3.293 Å and 3.957 Å. These large Tl-S distances are also the longest



Fig. 4 Isotropic displacement parameters B_{eq} (HA-MILTON, 1959) or B values are plotted versus the calculated valence sums (BROWN and ALTERMATT, 1985). Open symbols indicate outliers which were not employed for the calculation of mean values. The mean value of isotropic displacement parameters decreases from Tl⁺ to Bi³⁺.

in Fig. 1 and the weak TI-S interaction is reflected in the low calculated valence sums for Tl of 0.48 and 0.61 (Fig. 4). The other Tl outlier $(B_{eq} = 4.8)$ results from the structure of $Tl_2Sn_2S_3$ (DEL BUCCHIA et al., 1982) refined to R = 8.6%. In $Cu_{3.21}Bi_{4.79}S_9$ Ohmasa (1973) found two Bi positions to be only partially occupied but one position (Bi₃) with $B_{eq} = 3.7$ is assumed to be fully occupied. In general, unusually large displacement parameters can be caused by static (positional) disorder. In addition, NODA et al. (1983) noticed that in galena (PbS), the thermal parameter of Pb is larger than the one of S (as in most other sulfosalts) and determined significant enharmonic contributions of the Pb thermal motion.

References

- ARMBRUSTER, TH., and HUMMEL, W., (1987): (Sb,Bi,Pb) ordering in sulfosalts: Crystal-structure refinement of a Bi-rich izoklakeite. Amer. Miner. 72, 821-831.
- BALIĆ-ŽUNIĆ, T., and ENGEL, P. (1983): Crystal structure of synthetic PbTlAs₃S₆. Z. Kristallogr., 165, 261–269.
- BERGERHOFF, G., HUNDT, F., SIEVERS, R., and BROWN, I.D. (1983): The inorganic crystal structure data base. J. Chem. Inform. and Comp. Sci., 23, 66-69.
- BROWN, I.D., and ALTERMATT, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. Acta, Cryst. B41, 244-247.
- DEL BUCCHIA, S., JUMAS, J.C., PHILIPPOT, E., and MAURIN, M. (1981): Etude dans les systèmes SnS- Tl_2S . Structure cristalline de Tl_4SnS_3 . Rev. Chim. Miner., 18, 224–234.
- DEL BUCCHIA, S., JUMAS, J.C., PHILIPPOT, E., and MAURIN, M. (1982): Structure cristalline du sulfure d'étain(II) et de thallium(I) Tl₂Sn₂S₃. Z. anorg. allg. Chem. 487, 199-206.
 EULENBERGER, G. (1980): Darstellung und Kristall-
- EULENBERGER, G. (1980): Darstellung und Kristallstruktur des Dithallium(I) blei(II)tetrathiogermanats(IV). Z. Naturforsch., B35, 335-339.
- GOSTOJIĆ, M., EDENHARTER, A., NOWACKI, W., and ENGEL, P. (1982): The crystal structure of synthetic Tl₂MnAs₂S₅. Z. Kristallogr. 158, 43-51. HAMILTON, W.C. (1959): On the isotropic tempera-
- HAMILTON, W.C. (1959): On the isotropic temperature factor equivalent to a given anisotropic temperature factor. Acta. Cryst., 12, 609-610.
- perature factor. Acta. Cryst., 12, 609-610. KOCMAN, V., and NUFFIELD, E. W. (1973): The crystal structure of wittichenite, Cu₃BiS₃. Acta Cryst. B29, 2528-2535.
- LECLERC, B., and BAILLY, M. (1973): Structure cristalline du sulfure de thallium: Tl_4S_3 . Acta Cryst., B29, 2334-2336.
- MARUMO, F., and NOWACKI, W. (1965): The crystal structure of rathite-I. Z. Kristallogr., 122, 433-456.

- MARUMO, F. and NOWACKI, W., (1967): The crystal structure of hatchite, PbTlAgAs₂S₅. Z. Kristallogr., 125, 249–265.
- NAGL, Á. (1979): The crystal structure of a thallium sulfosalt, Tl₈Pb₄Sb₂₁As₁₉S₆₈. Z. Kristallogr., 150, 85-106.
- NAKAMURA, Y., ARUGA, A., NAKAI, I., and NAGA-SHIMA, K. (1984): The crystal structure of a new thiosilicate of thallium, TlInSiS₄. Bull. Chem. Soc. Jpn., 57, 1718-1722.
- NODA, Y. (1983): Charge distribution and atomic thermal vibration in lead chalcogenide crystals. Acta Cryst. B39, 312-317.
 NOWACKI, W., and BAHEZRE, C. (1963): Die Bestim-
- NOWACKI, W., and BAHEZRE, C. (1963): Die Bestimmung der chemischen Zusammensetzung einiger Sulfosalze aus dem Lengenbach (Binnatal, Kt. Wallis) mit Hilfe der elektronischen Mikrosonde. Schweiz. mineral. petrogr. Mitt., 43, 407-411.

- Онмаsa, M. (1973): The crystal structure of $Cu_{2+x}Bi_{6-x}S_9$ (x = 1.21). Neues Jahrb. Miner. Mh., 1973, 227-233.
- TAKÉUCHI, Y., GHOSE, S., and NOWACKI, W. (1965): The crystal structure of hutchinsonite, (Tl, Pb)₂As₅S₉. Z. Kristallogr. 212, 321-348.
- Takéuchi, Y., OHMASA, M., and Nowacki, W. (1968): The crystal structure of wallisite, PbTlCuAs₂S₅, the Cu analogue of hatchite, PbTlAgAs₂S₅. Z. Kristallogr., 127, 349-365.

Manuscript received October 27, 1987; completed manuscript accepted December 10, 1987.