## References

Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Gougeon, P. (1984). Thesis, Univ. of Rennes, France.

Gougeon, P., Padiou, J., Potel, M., Sergent, M. & Couach, M. (1984). *Ann. Chim. Fr.* **9**, 1083–1086.

Gougeon, P., Potel, M., Padiou, J. & Sergent, M. (1987). *Mater. Res. Bull.* **22**, 1087–1093.

Gougeon, P., Potel, M., Padiou, J. & Sergent, M. (1988). *Mater. Res. Bull.* **23**, 453–460.

Gougeon, P., Potel, M. & Sergent, M. (1989*a*). *Acta Cryst.* C**45**, 182–185.

Gougeon, P., Potel, M. & Sergent, M. (1989*b*). *Acta Cryst.* C**45**, 1413–1415.

Main, P., Fiske, S., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Stout, G. & Jensen, L. H. (1968). *X-ray Structure Determination*. London: Macmillan.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

*Acta Cryst.* (1990). C**46**, 2287–2291

# Structure of Antimony Lead Selenide, $Pb_4Sb_4Se_{10}$, a Selenium Analogue of Cosalite

By A. Skowron and I. D. Brown

*Institute for Materials Research, McMaster University,* 1280 *Main St West, Hamilton, Ontario,*
*Canada L*8*S* 4*M*1

(*Received* 18 *December* 1989; *accepted* 26 *March* 1990)

**Abstract.** $M_r$ = 2105·36, orthorhombic, *Pnam*, $a$ = 24·591 (8), $b$ = 19·757 (8), $c$ = 4·166 (8) Å, $V$ = 2024 Å$^3$, $Z$ = 4, $D_x$ = 6·91 g cm$^{-3}$, Mo $K\alpha$ radiation, $\lambda$ = 0·71069 Å, $\mu$ = 543·9 cm$^{-1}$, $F(000)$ = 3487, room temperature, $R$ = 0·064 for 1562 unique reflections. The crystal was prepared by slow cooling in vacuum sealed ampoules. The structure is isotypic with cosalite, $Pb_4Bi_4(Ag,Cu)S_{10}$, and is composed of ribbons built up of square pyramidal $(Pb,Sb)Se_5$ groups. The distribution of Sb/Pb atomic positions was determined by site occupancy refinement and, independently, by bond-valence analysis.

**Introduction.** We have previously undertaken determinations to establish the structural details, including cation distributions, of specific lead antimony sulfides (Skowron & Brown, 1990*a*,*b*,*c*). Here, the structure of a lead antimony selenide is investigated and compared with an isotypic lead bismuth sulfide. To obtain a broader view, the results are taken together with those from other works, and cation environments in a number of selenides and sulfides compared.

**Experimental.** Single crystals of $Pb_4Sb_4Se_{10}$ were prepared from elemental lead, antimony and selenium of 'Specpure' grade, supplied by Johnson Matthey Ltd. Six samples were prepared by weighing the elements in the proportions corresponding to 50–75 mol % of PbSe. The samples were then sealed in evacuated silica tubes, melted at 1073 K and subsequently slowly cooled over a period of two weeks to 823 K. Extensive phase separation into regions of acicular crystals was observed in all the ampoules. A needle-shaped crystal, 0·1 × 0·2 × 0·5 mm, which was chosen from the ampoule with the initial composition 55 mol % PbSe, was mounted with the needle axis along the goniometer axis for the X-ray study.

The unit-cell parameters were refined from the Bragg angles of 15 well centered reflections in the range $15 < 2\theta < 30°$ measured on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation, $\lambda$ = 0·71069 Å. Intensities of 5308 reflections were measured in the range $2\theta < 50°$ and $0 \leq h \leq 26$, $-20 \leq k \leq 20$, $-4 \leq l \leq 4$ with a $\theta/2\theta$ scan. Two standard reflections ($62\bar{1}$, $10,\bar{4},\bar{2}$), measured every 50 reflections, varied by ± 2·1%. The systematic absences, $0kl$: $k + l = 2n + 1$; $h0l$: $h = 2n + 1$, found using precession photographs, indicate space groups *Pnam* or $Pna2_1$. The former was chosen and led to a satisfactoryy refinement. The absorption correction was based on $\psi$ scans of 13 reflections (maximum correction was 6·29 for the intensity of the $1\bar{2}2$ reflection). The intensities were corrected for Lorentz and polarization effects. Equivalent reflections were averaged ($R_{\rm int}$ = 0·159 before and $R_{\rm int}$ = 0·049 after the absorption correction) to give 1562 unique reflections.

The initial atomic positions, found by direct methods using *SHELXS* (Sheldrick, 1986), were refined using *SHELX*76 (Sheldrick, 1976) by full-matrix least squares with anisotropic atomic displacement parameters for all the atoms and with mixed occupancies for the metal sites. Complex scat-

0108-2701/90/122287-05\$03.00

Table 1. *Percentage of* Sb (*or* Bi) *on cation sites in* $Pb_4Sb_4Se_{10}$ *and cosalite*

| | $Pb_4Sb_4Se_{10}$ | | Cosalite |
|---|---|---|---|
| | X-ray refinement* | Bond-valence method | Macicek (1988)† |
| $M(1)$ | 82 | 80 | 54 Bi + 12 Ag‡ |
| $M(2)$ | 0 | 0 | 0 |
| $M(3)$ | 0 | 0 | 0 |
| $M(4)$ | 32 | 33 | 23 |
| $M(5)$ | 88 | 75 | 100 |
| $M(6)$ | 60 | 46 | 23 |
| $M(7)$ | 88 | 80 | 100 |
| $M(8)$ | 92 | 86 | 100 |
| $M(9)$ | — | — | 30 Cu§ |
| $M(10)$ | — | — | 24 Cu¶ |
| Formula | $Pb_{3{\cdot}58}Sb_{4{\cdot}42}Se_{10}$ | $Pb_4Sb_4Se_{10}$ | $Ag_{0{\cdot}12}Cu_{0{\cdot}54}Pb_{3{\cdot}54}Bi_4S_{10}$ |

* Standard uncertainties estimated by *SHELX*76 are 1% but are probably at least a factor of 10 too small.

† Determined by bond-valence method.

‡ This site does not contain lead (it is 34% vacant).

§ A mixture of $Cu^{2+}$ (52%) and $Cu^{1+}$ (48%) is assumed on this site.

¶ $Cu^+$ is assumed on this site.

Table 2. *Crystal structures selected for the calculation of* $r_0$ *for* Sb—Se *and* Pb—Se *bonds*

The structures used in Fig. 3 are labelled with *.

| | No. of positions | $r_0$(Å)† | Reference |
|---|---|---|---|
| *$BaBiSe_3$ | 2 | | (*a*) |
| *$Bi_2Se_3$ | 2 | | (*b*) |
| *$AgBiSe_2$ | 2 | | (*c*) |
| *$PbAl_2Se_4$ | 1 | 2·697 | (*d*) |
| *$PbGa_2Se_4$ | 3 | 2·708, 2·708, 2·650 | (*d*) |
| *$Pb_xMo_3Se_4$ | 1 | 2·664 | (*e*) |
| *$PbU_2Se_5$ | 1 | 2·663 | (*f*) |
| *PbSe | 1 | 2·661 | (*g*) |
| *$Sb_2Se_3$ | 2 | 2·583, 2·577 | (*h*) |
| $KSbSe_2$ | 2 | 2·577, 2·578 | (*i*) |
| $BaSb_2Se_4$ | 4 | 2·589, 2·610, 2·625, 2·623 | (*j*) |
| $CsSbSe_2$ | 2 | 2·529‡, 2·616 | (*k*) |

References: (*a*) Volk, Cordier & Schäfer (1980); (*b*) Atabaeva, Mashkov & Popova (1973); (*c*) Geller & Wernick (1959); (*d*) Klee & Schäfer (1980); (*e*) Guillevic, Lestrat & Grandjean (1967); (*f*) Potel, Brochu & Padion (1975); (*g*) Earley (1950); (*h*) Tideswell *et al.* (1957); (*i*) Dittmar & Schäfer (1977); (*j*) Cordier & Schäfer (1979); (*k*) Kanishcheva, Mikhailov, Lazarev & Moshchalkova (1980).

† Values of $r_0$ were those that gave valence sums of two at Pb or three at Sb using equation (1). The values of $r_0$ used in this study were the averages of those listed.

‡ Rejected from the calculation of the mean value of $r_0$.

tering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1.). $F^2$'s were weighted by $w = k/[\sigma^2(F_o) + gF_o^2]$, where $\sigma(F_o)$ was the uncertainty derived from the counting statistics and $k$ and $g$ were parameters that refined to 6·5 and 0·0006 respectively. The Pb occupation numbers of sites 1 and 3 quickly refined to values close to 1·0 and were kept fixed at this value in the subsequent stages of the refinement. The refinement converged to $wR = 0{\cdot}057$, $R = 0{\cdot}062$ and $S = 1{\cdot}50$.

The program did not permit a constraint to be put on the total number of Pb or Sb atoms in the unit cell and the refined occupation numbers, shown in column two of Table 1, result in a formula of $Pb_{3{\cdot}58}Sb_{4{\cdot}42}Se_{10}$ which is different from the expected electrically neutral formula $Pb_4Sb_4Se_{10}$. In order to clarify this discrepancy we determined an independent set of occupation numbers using the bond-valence method described by Skowron & Brown (1990*a*). In this we use the refined atomic parameters to calculate bond lengths ($r$) from which bond valences ($s$) were calculated using the equation:

$$s = \exp[(r_0 - r)/0{\cdot}37], \qquad (1)$$

where $r_0$ was determined for Sb—Se (2·598 Å) and Pb—Se (2·679 Å) bonds using the published crystal structures of compounds which contained these bonds but which contained neither Se—Se, metal–metal bonds nor any kind of disorder. Table 2 summarizes chemical composition and references for these structures. The occupation numbers obtained correspond to the nearly correct formula $Pb_{4{\cdot}07}Sb_{3{\cdot}93}Se_{10}$. An exactly electroneutral formula was obtained by changing $r_0$(Sb—Se) to 2·602 Å. The valence analysis using this value of $r_0$ is presented in Table 3 and the occupation numbers inferred from this analysis in column three of Table 1.

Because the occupation numbers determined from the bond valences correspond to an electrically neutral crystal we consider these values to be more reliable. We used them as fixed parameters in *SHELX*76 and refined all positional and atomic displacement parameters to obtain $wR = 0{\cdot}059$, $R = 0{\cdot}064$ and $S = 1{\cdot}58$. Maximum final shift/e.s.d. = 0·072, mean = 0·017, maximum density in the final difference Fourier map = 2·81, minimum = $-3{\cdot}11$ e Å$^{-3}$. This refinement was used to generate the final atomic coordinates listed in Table 4. The interatomic distances are given in Table 5.*

**Discussion.** The structure of $Pb_4Sb_4Se_{10}$ (Figs. 1 and 2) is composed of ribbons (shaded in Fig. 2) made of back to back square pyramidal $(Pb,Sb)Se_5$ groups. The ribbons extend indefinitely in the **c** direction, are one pyramid thick and their width equals four times the basal distance of the $(Pb,Sb)Se_5$ pyramid. They can be obtained from the unit ribbon, $Sb_4Se_6$, found

---

* A Standard Crystallographic File (Brown, 1983) has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53164 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Valence analysis in* $Pb_4Sb_4Se_{10}$

The bond valences are an average of valences calculated as Pb—Se and Sb—Se weighted according to X-ray occupation number. *V* is the atomic valence similarly weighted.

| | *M*(1) | *M*(2) | *M*(3) | *M*(4) | *M*(5) | *M*(6) | *M*(7) | *M*(8) | $\sum s$ |
|---|---|---|---|---|---|---|---|---|---|
| %Sb | 82 | 0 | 0 | 32 | 88 | 60 | 88 | 92 | |
| Se(1) | 0·49 | | 0·10 × 2 | | | | | 0·55 × 2 | −1·79 |
| Se(2) | | 0·28 | | | | | 0·43 × 2 | 0·33 × 2 | −1·80 |
| Se(3) | | | 0·43 | | | 0·26 × 2 | 0·45 × 2 | | −1·85 |
| Se(4) | | | | 0·38 | 0·18 × 2 | 0·51 × 2 | 0·14 | | −1·90 |
| Se(5) | | 0·18 × 2 | | 0·43 × 2 | 0·88 | | | | −2·12 |
| Se(6) | | | 0·35 × 2 | 0·34 × 2 | | 0·78 | | | −2·16 |
| Se(7) | | 0·31 × 2 | 0·32 × 2 | | | | 0·84 | | −2·10 |
| Se(8) | 0·33 × 2 | 0·28 × 2 | | | | | | 0·79 | −2·01 |
| Se(9) | 0·38 + 0·62 × 2 | | | 0·43 | | | | | −2·05 |
| Se(10) | | 0·18 | 0·09 | | 0·69 × 2 | | | 0·25 | −1·90 |
| $\sum s$ | 2·77 | 2·00 | 2·06 | 2·35 | 2·62 | 2·32 | 2·61 | 2·80 | |
| *V* | 2·82 | 2·00 | 2·00 | 2·32 | 2·88 | 2·60 | 2·88 | 2·92 | |

Table 4. *Atomic coordinates and equivalent isotropic displacement parameters for* $Pb_4Sb_4Se_{10}$

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

| | $x$ | $y$ | $z$ | $U_{eq}$(Å$^2$) |
|---|---|---|---|---|
| *M*(1) | 0·4359 (1) | 0·5389 (1) | 0·75 | 0·027 (1) |
| *M*(2) | 0·2954 (1) | 0·3910 (1) | 0·75 | 0·033 (1) |
| *M*(3) | 0·1273 (1) | 0·2976 (1) | 0·75 | 0·031 (1) |
| *M*(4) | 0·0434 (1) | 0·7710 (1) | 0·25 | 0·021 (1) |
| *M*(5) | 0·1741 (1) | 0·6872 (1) | 0·75 | 0·023 (1) |
| *M*(6) | 0·0099 (1) | 0·5912 (1) | 0·75 | 0·028 (1) |
| *M*(7) | 0·1560 (1) | 0·4841 (1) | 0·25 | 0·024 (1) |
| *M*(8) | 0·3034 (1) | 0·5929 (1) | 0·25 | 0·022 (1) |
| Se(1) | 0·3641 (1) | 0·6548 (2) | 0·75 | 0·036 (2) |
| Se(2) | 0·2310 (1) | 0·5296 (2) | 0·75 | 0·022 (2) |
| Se(3) | 0·0821 (1) | 0·4380 (2) | 0·75 | 0·018 (2) |
| Se(4) | 0·0855 (1) | 0·6275 (2) | 0·25 | 0·021 (2) |
| Se(5) | 0·1249 (1) | 0·8069 (2) | 0·75 | 0·024 (2) |
| Se(6) | 0·0346 (1) | 0·2833 (2) | 0·25 | 0·026 (2) |
| Se(7) | 0·2043 (1) | 0·3628 (2) | 0·25 | 0·029 (2) |
| Se(8) | 0·3614 (1) | 0·4774 (2) | 0·25 | 0·026 (2) |
| Se(9) | 0·5002 (2) | 0·5886 (2) | 0·25 | 0·026 (2) |
| Se(10) | 0·2390 (1) | 0·7289 (2) | 0·25 | 0·034 (2) |

Table 5. *Interatomic distances* (Å) *less than* 3·6 Å *in* $Pb_4Sb_4Se_{10}$

| | | |
|---|---|---|
| *M*(1)—Se(9) | × 2 | 2·793 (3) |
| Se(1) | | 2·879 (4) |
| Se(9) | | 2·970 (4) |
| Se(8) | × 2 | 3·028 (3) |
| *M*(2)—Se(7) | × 2 | 3·109 (2) |
| Se(8) | × 2 | 3·146 (3) |
| Se(2) | | 3·163 (4) |
| Se(5) | × 2 | 3·308 (3) |
| Se(10) | | 3·313 (4) |
| *M*(3)—Se(3) | | 2·989 (4) |
| Se(6) | × 2 | 3·069 (2) |
| Se(7) | × 2 | 3·096 (2) |
| Se(1) | × 2 | 3·528 (3) |
| Se(10) | | 3·557 (3) |
| *M*(4)—Se(9) | | 2·969 (4) |
| Se(5) | × 2 | 2·976 (2) |
| Se(4) | | 3·019 (5) |
| Se(6) | × 2 | 3·055 (2) |
| *M*(5)—Se(5) | | 2·656 (4) |
| Se(10) | × 2 | 2·750 (4) |
| Se(4) | × 2 | 3·236 (3) |
| Se(2) | | 3·415 (4) |
| *M*(6)—Se(6) | | 2·728 (4) |
| Se(4) | × 2 | 2·883 (3) |
| Se(3) | × 2 | 3·131 (3) |
| Se(3) | | 3·509 (4) |
| *M*(7)—Se(7) | | 2·673 (4) |
| Se(3) | × 2 | 2·908 (3) |
| Se(2) | × 2 | 2·923 (3) |
| Se(4) | | 3·324 (4) |
| *M*(8)—Se(8) | | 2·692 (4) |
| Se(1) | × 2 | 2·830 (3) |
| Se(2) | × 2 | 3·011 (3) |
| Se(10) | | 3·118 (4) |

in $Sb_2Se_3$ (Tideswell, Kruse & McCullough, 1957), by splitting the $Sb_4Se_6$ ribbon and incorporating four $PbSe_5$ pyramids into the middle. The stoichiometry, determined by the number of PbSe units introduced in the ribbon, is: $Sb_2Se_3 + (PbSe)_4 + Sb_2Se_3 = Pb_4Sb_4Se_{10}$.

Two parallel ribbons combine to form a ribbon pair in which metal atoms on the facing sides of the ribbons are six coordinated. On the other sides of the ribbons two sites are eight coordinated and the other two six coordinated. The Sb atoms are only found on the six-coordinated sites. As a result each ribbon pair is rich in lead on the outside and rich in antimony on the inside. All cation sites show the distortions expected from stereoactive lone electron pairs.

$Pb_4Sb_4Se_{10}$ is isotypic with cosalite (Srikrishnan & Nowacki, 1974; Macicek, 1988), traditionally given the idealized formula $Pb_4Bi_4S_{10}$. Although both have the same geometrical framework, cosalite contains additional Cu atoms in sites near the edges of the ribbons and also differs in the details of the metal occupancies (Macicek, 1988), see column four of Table 1. The two cation sites which are eight coordinated are fully occupied by lead in both structures. In the selenide, mixed occupancies are found in the remaining six sites, four of which contain mostly antimony.

Armbruster & Hummel (1987) have examined the environments of lead, bismuth and antimony in a number of sulfides to study the distortion of the cation coordination polyhedra caused by the influence of the lone electron pair. To measure this distortion and to compare the sizes of the environments around the cations they plot the mean of the three shortest interatomic distances against the mean of the two next shortest.

We have constructed a similar diagram for lead, antimony and bismuth in selenides, Fig. 3, using only the sites in the compounds listed in Table 2 that have coordination numbers greater than four. We used three structures with Bi (six Bi sites) and five structures with Pb (seven Pb sites). The only suitable compound containing Sb in higher than four coordination was $Sb_2Se_3$ (two Sb sites). In Fig. 3 we compare our results with those of Armbruster & Hummel after correcting for the difference in size of the Se and S atoms ($r_{Se} - r_S = 0{\cdot}13$ Å).

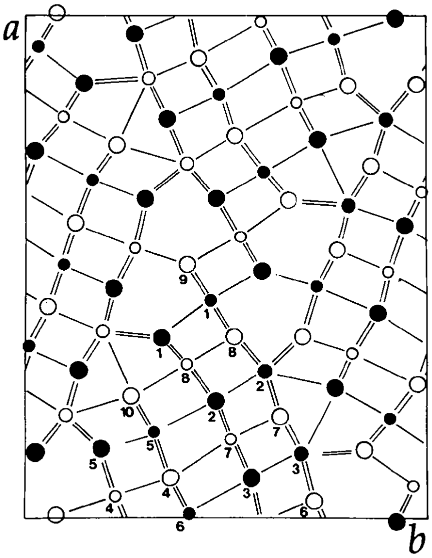

Fig. 1. The unit cell of $Pb_4Sb_4Se_{10}$ projected down [001]. In order of decreasing size, the circles denote Se, Pb and mixed sites. Atoms at $z = 0{\cdot}25$ and $z = 0{\cdot}75$ are indicated by open and filled circles respectively.

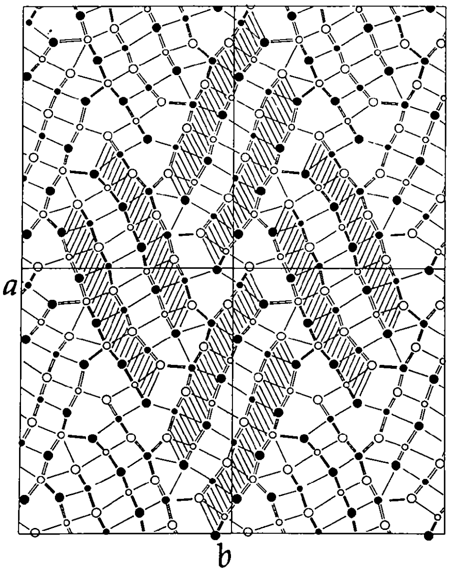

Fig. 2. Four unit cells of the crystal structure of $Pb_4Sb_4Se_{10}$ projected down [001] with the ribbons indicated by shading. Conventions for indicating the atoms are the same as in Fig. 1.

Good agreement between distortion fields of sulfides and selenides can be reached if the Armbruster & Hummel region of Sb is extended to include regular coordinations (dashed line in Fig. 3). The octahedral sites in cosalite (Macicek, 1988) and in $Pb_4Sb_4Se_{10}$ lie in the same part of the diagram, a part which corresponds to short Bi—S and long Sb—Se distances but with comparable distortion.

Macicek (1988) points out that copper and silver play an important role in stabilizing cosalite as the phase cannot be synthesized in the Pb–Bi–S system without their presence. Chang, Walia & Knowles (1980), on the other hand, reported the synthesis of a phase with composition $Pb_2(Bi_{0{\cdot}8}Sb_{0{\cdot}2})_2S_5$ which they identified as cosalite from its powder diffraction pattern. However, the cosalite analogue grows readily in the undoped Pb–Sb–Se system. The tolerance on the size of metals that can be incorporated into cosalite is apparently not very large. It seems that the 'ideal' cation to form the structure is one that prefers a weakly distorted environment, and that is bigger than antimony but smaller than bismuth. In this respect, antimony in the selenide has an advantage over bismuth in sulfide, since it can, by

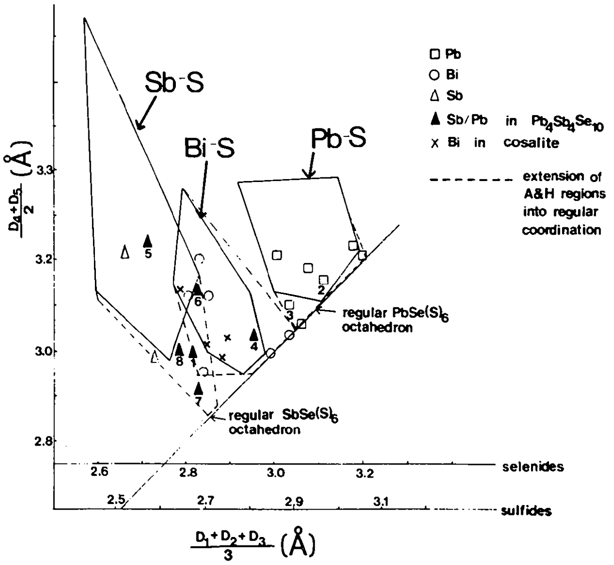

Fig. 3. The mean value of the three shortest $M$—Se distances *vs* the mean value of the next two shortest. The distances are obtained from the published structures of compounds labelled with * in Table 2. The distortion fields for Pb, Sb and Bi coordination polyhedra in sulfides are indicated with solid lines (after Armbruster & Hummel, 1987). The distortion fields for $M$—Se bonds are drawn in broken lines.

partial occupation with lead, adapt to the necessary metal size. Bismuth, however, needs substitution by a smaller cation to reduce its average size. As a result stabilizers, like copper or silver, or substitution by antimony are necessary in the sulfide. In the structure obtained by Macicek the Bi is replaced on half the No. 1 sites by either Ag or one or two Cu atoms at nearby interstitial positions.

We are indebted to Dr J. Macicek for letting us quote his results prior to publication and to the National Science and Engineering Research Council of Canada for an operating grant. R. Faggiani's help in the data collection is also gratefully acknowledged.

### References

Armbruster, T. & Hummel, W. (1987). *Am. Mineral.* **72**, 821–831.

Atabaeva, E. Ya., Mashkov, S. A. & Popova, S. V. (1973). *Kristallografiya*, **8**, 173–174.

Brown, I. D. (1983). *Acta Cryst.* A**39**, 216–224.

Chang, L. L. Y., Walia, D. S. & Knowles, C. R. (1980). *Econ. Geol.* **75**, 317–328.

Cordier, G. & Schäfer, H. (1979). *Z. Naturforsch. Teil B*, **34**, 1053–1056.

Dittmar, G. & Schäfer, H. (1977). *Z. Naturforsch. Teil B*, **32**, 1346–1348.

Earley, J. W. (1950). *Am. Mineral.* **35**, 338–350.

Geller, S. & Wernick, J. H. (1959). *Acta Cryst.* **12**, 46–54.

Guillevic, P. J., Lestrat, H. & Grandjean, D. (1967). *Acta Cryst.* B**32**, 1342–1345.

Kanischeva, A. S., Mikhailov, Yu. N., Lazarev, V. B. & Moshchalkova, N. A. (1980). *Dokl. Akad. Nauk SSSR*, **252**, 872–875.

Klee, W. & Schäfer, H. (1980). *Mater. Res. Bull.* **15**, 1033–1038.

Macicek, J. (1988). Private communication.

Potel, M., Brochu, R. & Padion, J. (1975). *Mater. Res. Bull.* **10**, 206.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.

Skowron, A. & Brown, I. D. (1990*a*). *Acta Cryst.* C**46**, 527–531.

Skowron, A. & Brown, I. D. (1990*b*). *Acta Cryst.* C**46**, 531–534.

Skowron, A. & Brown, I. D. (1990*c*). *Acta Cryst.* C**46**, 534–536.

Srikrishnan, T. & Nowacki, W. (1974). *Z. Kristallogr.* **140**, 114–136.

Tideswell, N. W., Kruse, F. H. & McCullough, J. D. (1957). *Acta Cryst.* **10**, 99–102.

Volk, K., Cordier, G. & Schäfer, H. (1980). *Z. Naturforsch. Teil B*, **35**, 134–140.

*Acta Cryst.* (1990). C**46**, 2291–2294

# Clinoclase and the Geometry of [5]-Coordinate Cu$^{2+}$ in Minerals

By Ray K. Eby* and Frank C. Hawthorne

*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2*

(*Received* 15 *March* 1990; *accepted* 11 *April* 1990)

**Abstract.** Tricopper arsenate trihydroxide, Cu$_3$(AsO$_4$)(OH)$_3$, $M_r = 380{\cdot}58$, monoclinic, $P2_1/c$, $a = 7{\cdot}257$ (2), $b = 6{\cdot}457$ (2), $c = 12{\cdot}378$ (3) Å, $\beta = 99{\cdot}51$ (2)°, $V = 572{\cdot}0$ (3) Å$^3$, $Z = 4$, $D_x = 4{\cdot}42$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu$ = 175 cm$^{-1}$, $F(000) = 716$, $T = 297$ K, $R = 0{\cdot}044$ for 1404 observed reflections. The structure is a heteropolyhedral framework of AsO$_4$ tetrahedra, CuO$_3$(OH)$_3$ octahedra and CuO$_2$(OH)$_3$ square pyramids. [5]-coordinated Cu$^{2+}$ is common in minerals, and the salient features of square pyramidal and trigonal bipyramidal coordinations are examined in these structures.

**Introduction.** We have a systematic study of the stereochemistry of Cu$^{2+}$ oxysalt minerals currently underway (Eby & Hawthorne, 1989*a*,*b*; Hawthorne & Eby, 1985; Hawthorne & Groat, 1985, 1986; Hawthorne, 1985*a*,*b*, 1986*a*,*b*; Groat & Hawthorne, 1987; Hawthorne, Groat & Eby, 1989), focused primarily on the heteropolyhedral connectivity of these structures, and the interaction between local Jahn–Teller distortion, polyhedral connectivity and structural periodicity. As part of this work, a refinement and reconsideration of the structure of clinoclase was initiated.

**Experimental.** Clinoclase from Roughton Gill, England, National Mineral Collection catalogue number 18291, was obtained from the Geological Survey of Canada. Crystal size: 0·24 × 0·28 × 0·32 mm; unit-cell parameters refined from 25 reflections ($5 < \theta < 15°$) automatically aligned on a Nicolet $R3m$ diffractometer at 297 K. Data collection: 1187 reflections, $3 < 2\theta < 60°$, $h$ 0 − 13, $k$ 0–14,

---

* Present address: Department of Geological Sciences, University of New Mexico, Albuquerque, New Mexico 87131, USA.

0108-2701/90/122291-04$03.00