

## Crystal structures of chalcostibite (CuSbS<sub>2</sub>) and emplectite (CuBiS<sub>2</sub>): Structural relationship of stereochemical activity between chalcostibite and emplectite

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### ABSTRACT

The crystal structures of chalcostibite CuSbS<sub>2</sub> (orthorhombic, space group *Pnma*,  $a = 6.018(1)$ ,  $b = 3.7958(6)$ , and  $c = 14.495(7)$  Å,  $V = 331.1(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $R1 = 0.040$ ,  $wR2 = 0.155$  for 533 reflections) and emplectite CuBiS<sub>2</sub> (orthorhombic, space group *Pnma*,  $a = 6.134(1)$ ,  $b = 3.9111(8)$ , and  $c = 14.548(8)$  Å,  $V = 348.8(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $R1 = 0.037$ ,  $wR2 = 0.112$  for 492 reflections) were redetermined using a four-circle diffractometer and graphite-monochromatized MoK $\alpha$  radiation. These two crystal structures are composed of *MS*<sub>5</sub> square pyramids ( $M = \text{Sb}$  and  $\text{Bi}$ ) and nearly regular CuS<sub>4</sub> tetrahedra. The five *M*-S bond distances in the SbS<sub>5</sub> square pyramid in chalcostibite are always shorter than corresponding distances in the BiS<sub>5</sub> square pyramid in emplectite because the Sb atom is smaller than the Bi atom. The *a* cell parameter increases appreciably from chalcostibite to emplectite not only because of increasing *M*-S bond distances in the *MS*<sub>5</sub> square pyramid, but also because of increasing Cu-S<sub>2</sub>-Cu bond angles along **a**. The increase in the *b* cell parameter is caused mainly by increasing *M*-S bond distances along **b**. In contrast, the slight increase of the *c* cell parameter is largely brought about by decreasing Cu-S<sub>2</sub>-Cu bond angles ascribed to weakened stereochemical activity of Bi 6s<sup>2</sup> lone-pair electrons. The anisotropic change of unit-cell parameters from chalcostibite to emplectite is strongly associated with the positions of the lone-pair electrons in the unit cell.

### INTRODUCTION

Chalcostibite CuSbS<sub>2</sub> and emplectite CuBiS<sub>2</sub> are isostructural (Hofmann 1933; Portheine and Nowacki 1975; Razmara et al. 1997). Their structures comprise square pyramids of Sb (or Bi) linked to form chains of SbS<sub>2</sub> (or BiS<sub>2</sub>) along **b** and CuS<sub>4</sub> tetrahedra forming chains of CuS<sub>3</sub> parallel to **b** (Razmara et al. 1997). These two types of infinite chains are linked to form sheets that are perpendicular to **c** (Portheine and Nowacki 1975; Razmara et al. 1997). These structures can be imagined as being made up of slices of the SnS-like structure parallel to (101) and (10 $\bar{1}$ )<sub>SnS</sub> twinned on the median plane (Makovicky 1985). Razmara et al. (1997) demonstrated that the slight variation of the *c* cell parameter from chalcostibite [14.499(3) Å] to emplectite [14.524(2) Å] is ascribed to inflexible linkages between the SbS<sub>2</sub> (or BiS<sub>2</sub>) + CuS<sub>3</sub> sheets perpendicular to **c**. However, structural refinements of both chalcostibite and emplectite reported by Razmara et al. (1997) yielded high values of the *R* factor ( $R_1 = 26.8\%$ ,  $R_{wp} = 23.5\%$  for chalcostibite;  $R_1 = 14.9\%$ ,  $R_{wp} = 20.2\%$  for emplectite) and poor accuracy for the atomic positions. Therefore, it is impossible to accurately compare the highly anisotropic bondings of the Sb coordination with those of Bi coordination. For this reason, the structures of chalcostibite and emplectite have been re-refined. The present work particularly addresses stereochemical activity of the Sb 5s<sup>2</sup> and Bi 6s<sup>2</sup> lone-pair electrons.

### EXPERIMENTAL METHODS

The samples of chalcostibite and emplectite used in this study are from Rar el Anz, east of Casablanca, Morocco, and Kaerfersteige, Schwarzwald, Germany. Chemical compositions of the crystals were analyzed quantitatively by electron microprobe (Superprobe JXA-8600; JEOL), with an acceleration voltage of 25 kV and a beam current of 10 nA. The natural and synthetic standards used were as follows: Cu metal (CuK $\alpha$ ), stibnite (SbL $\alpha$ ), Bi<sub>2</sub>Te<sub>3</sub> (BiM $\alpha$ ), and pyrite (SK $\alpha$ ). Microprobe analyses showed no marked deviation from ideal compositions. Trace metals (e.g., Ag, As, and Pb) were less than their detection limits of 0.1 wt%.

Single crystals suitable for intensity data collection were fixed on a glass capillary 0.1 mm in diameter and mounted on a four-circle diffractometer (CAD4; Enraf-Nonius B.V., Netherlands) using graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å). The unit-cell parameters were carefully measured and determined accurately from a least-squares fit to the corrected setting angles of 25 reflections between  $10^\circ \leq \theta \leq 13^\circ$  (Table 1). Diffraction data were collected at room temperature up to  $\theta = 30^\circ$ . Data reduction, including background and Lorentz polarization correction, was carried out with the SDP program system (Enraf-Nonius 1983). An empirical absorption correction using the  $\psi$ -scan technique was applied. Structural refinements were performed with the SHELXL-97 program (Sheldrick 1997). Several refinement cycles were carried out using first isotropic, then anisotropic thermal displacement parameters. The final *R1* values converged to 0.040 for 533 unique reflections and 0.037 for 492 unique reflections. Table 2 summarizes crystallographic data and the details of the refinements. Tables 3 and 4 list atomic coordinates, atomic displacement parameters, and selected bond distances and angles.

### RESULTS AND DISCUSSION

The main parts of the crystal structures of chalcostibite and emplectite that have been described previously (Portheine and Nowacki 1975; Razmara et al. 1997) are consistent with the results of the present refinements. However, the details of the interatomic bond distances and angles have been clarified.

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Table 4 shows that Cu atoms in chalcostibite and emplectite are surrounded by four S atoms in a nearly regular tetrahedron. In addition, the average Cu-S distance of 2.322 Å in chalcostibite agrees approximately with that of 2.324 Å in emplectite. On the other hand, the Sb-S bond distances in the SbS<sub>5</sub> square pyramid in chalcostibite are apparently shorter than the corresponding Bi-S bond distances (Table 4). This is because the Sb atom is smaller than the Bi atom (Shannon 1976). The difference in size between Sb and Bi atoms can account for the observation that the *b* cell parameters increase appreciably from chalcostibite to emplectite (Table 2) because along *b* these two structures consist mainly of the five *M*-S bonds (Figs. 1 and 2).

According to Valence Shell Electron Pair Repulsion (VSEPR) theory (Gillespie and Nyholm 1957), Sb or Bi atoms containing lone-pair electrons should form coordination environments in which the lone-pair electrons occupy one bonding site, yielding, for six coordination, five bonds to the S atoms arranged in a square pyramid and one vacant site occupied by the lone-pair electrons (Olivier-Fourcade et al. 1990). That is, the stereoactive lone-pair electrons in chalcostibite and emplectite can be regarded as directed toward the one missing atom at one edge of the MS<sub>5</sub>E octahedron, which is nearly perpendicular to *c* (Figs.

1 and 2). The Sb 5s<sup>2</sup> lone-pair electrons have a more obvious stereochemical activity than Bi 6s<sup>2</sup> lone-pair electrons (Pitzer 1979; Pykkö and Desclaux 1979). The Cu atoms are repelled more by the Sb 5s<sup>2</sup> lone-pair electrons (Fig. 1) than by the Bi 6s<sup>2</sup> lone-pair electrons (Fig. 2); the closest Sb-Cu distance [3.420(3) Å] becomes approximately equal to the closest Bi-Cu distance [3.419(5) Å] despite the shorter Sb-S bond distances in chalcostibite.

The stereochemical activity of the Sb 5s<sup>2</sup> lone-pair electrons considerably affects the geometry of the rigid CuS<sub>4</sub> tetrahedra. The Cu-S<sub>2</sub>-Cu bond angle in chalcostibite [109.1(1)°] is manifestly smaller than that in emplectite [111.2(2)°], whereas the Sb-S<sub>2</sub>-Cu bond angle in chalcostibite [122.2(4)°] is larger than the Bi-S<sub>2</sub>-Cu bond angle in emplectite [120.9(1)°] (Figs. 1 and 2). These variations indicate that the rigid CuS<sub>4</sub> tetrahedron in chalcostibite is rotated by repulsion with the Sb 5s<sup>2</sup> stereoactive lone-pair electrons. Figures 1 and 2 show that rotation of the CuS<sub>4</sub> tetrahedron results in an increase of the secondary bond distance between Sb and S1 along *c* [4.992(4) Å] as compared to the corresponding distance in emplectite [4.971(7) Å]. The low expansion characteristics along *c* for chalcostibite with respect to emplectite (Razmara et al. 1997) result from the competing

**TABLE 1.** X-ray diffraction data for chalcostibite and emplectite and calculated unit-cell parameters

			Chalcostibite		Emplectite	
			<i>a</i> = 6.018(1) Å	<i>a</i> = 6.134(1) Å	<i>a</i> = 6.134(1) Å	<i>a</i> = 6.134(1) Å
			<i>b</i> = 3.7958(6) Å	<i>b</i> = 3.9111(8) Å	<i>b</i> = 3.9111(8) Å	<i>b</i> = 3.9111(8) Å
			<i>c</i> = 14.495(7) Å	<i>c</i> = 14.540(8) Å	<i>c</i> = 14.540(8) Å	<i>c</i> = 14.540(8) Å
<i>h</i>	<i>k</i>	<i>l</i>	$\theta_{\text{obs}}$	$\theta_{\text{calc}}$	$\theta_{\text{obs}}$	$\theta_{\text{calc}}$
0	2	0	10.779	10.770	10.441	10.449
0	2	0	10.767	10.770	10.452	10.449
2	1	5	11.178	11.179	11.008	11.009
2	1	5	11.186	11.179	11.010	11.009
2	1	5	11.178	11.179	11.015	11.009
2	1	5	11.177	11.179	11.015	11.009
2	1	5	11.177	11.179	11.013	11.009
3	1	1	11.616	11.622	11.368	11.375
3	1	1	11.634	11.622	11.378	11.375
3	1	1	11.617	11.622	11.376	11.375
3	1	1	11.629	11.622	11.372	11.375
3	1	1	11.619	11.622	11.376	11.375
3	0	4	11.657	11.659	11.476	11.479
3	0	4	11.664	11.659	11.481	11.479
3	0	4	11.655	11.659	11.471	11.479
3	0	4	11.659	11.659	11.481	11.479
1	2	4	12.651	12.652	12.343	12.351
1	2	4	12.657	12.652	12.341	12.351
1	2	4	12.650	12.652	12.344	12.351
1	2	4	12.653	12.652	12.361	12.351
1	2	4	12.646	12.652	12.350	12.351
2	2	0	12.763	12.764	12.419	12.420
2	2	0	12.768	12.764	12.422	12.420
2	2	0	12.758	12.764	12.422	12.420
2	2	0	12.760	12.764	12.434	12.420

**TABLE 3.** Atomic coordinates and displacement parameters (Å<sup>2</sup>)

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
<b>Chalcostibite</b>										
Sb	0.2260(2)	0.25	0.06333(7)	0.0241(6)	0.0249(9)	0.0243(9)	0.0229(9)	0.0000	0.0011(2)	0.0000
Cu	0.7478(3)	0.75	0.1724(1)	0.0300(7)	0.0308(11)	0.0312(13)	0.0281(13)	0.0000	0.0010(6)	0.0000
S1	0.6221(5)	0.25	0.0950(2)	0.0229(8)	0.0222(15)	0.0242(15)	0.0225(15)	0.0000	0.0004(11)	0.0000
S2	0.1294(6)	0.75	0.1756(2)	0.0231(8)	0.0251(16)	0.0245(15)	0.0197(14)	0.0000	0.0001(11)	0.0000
<b>Emplectite</b>										
Bi	0.2315(1)	0.25	0.06294(7)	0.0271(4)	0.0250(6)	0.0270(7)	0.0293(6)	0.0000	0.0009(3)	0.0000
Cu	0.7508(5)	0.75	0.1721(3)	0.0322(8)	0.0274(18)	0.0354(20)	0.0338(17)	0.0000	0.0006(12)	0.0000
S1	0.6353(11)	0.25	0.0976(4)	0.0271(13)	0.0268(30)	0.0273(28)	0.0271(28)	0.0000	0.0027(22)	0.0000
S2	0.1261(10)	0.75	0.1774(4)	0.0263(12)	0.0225(28)	0.0271(28)	0.0292(28)	0.0000	0.0004(21)	0.0000

**TABLE 2.** Summarized crystal data and details of the refinement parameters

	Chalcostibite	Emplectite
Chemical formula	CuSb <sub>5</sub> S <sub>2</sub>	CuBi <sub>5</sub> S <sub>2</sub>
Temperature	293 K	293 K
Formula weight	249.42	336.65
Crystal dimensions	0.60 × 0.40 × 0.20 mm	0.40 × 0.05 × 0.05 mm
Crystal system	orthorhombic	orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>
<i>a</i>	6.018(1) Å	6.134(1) Å
<i>b</i>	3.7958(6) Å	3.9111(8) Å
<i>c</i>	14.495(7) Å	14.540(8) Å
<i>V</i>	331.1(1) Å <sup>3</sup>	348.8(2) Å <sup>3</sup>
<i>Z</i>	4	4
2 $\theta_{\text{max}}$	59.88°	59.89°
Index ranges	0 ≤ <i>h</i> ≤ 8 0 ≤ <i>k</i> ≤ 5 0 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 8 0 ≤ <i>k</i> ≤ 5 0 ≤ <i>l</i> ≤ 20
<i>D</i> <sub>calc</sub>	5.004 g/cm <sup>3</sup>	6.410 g/cm <sup>3</sup>
Absorption coefficient (MoK $\alpha$ )	15.54 mm <sup>-1</sup>	57.38 mm <sup>-1</sup>
<i>F</i> (000)	448.00	576.00
Collected reflections	617	651
Unique reflections	548	578
Observed reflections [ <i>F</i> <sub>o</sub> > 4 $\sigma$ ( <i>F</i> <sub>o</sub> )]	533	492
Parameters used in the refinement	25	25
<i>R</i> <sub>w</sub>	0.013	0.057
<i>R</i> 1 [ <i>F</i> <sub>o</sub> > 4 $\sigma$ ( <i>F</i> <sub>o</sub> )]	0.040	0.037
<i>R</i> 1 (all data)	0.043	0.049
<i>wR</i> 2 [ <i>F</i> <sub>o</sub> > 4 $\sigma$ ( <i>F</i> <sub>o</sub> )]	0.155	0.112
Goodness of Fit	1.29	1.28
Final $\Delta\rho_{\text{max}}$	2.54 e/Å <sup>3</sup>	2.88 e/Å <sup>3</sup>
Final $\Delta\rho_{\text{min}}$	-1.94 e/Å <sup>3</sup>	-1.63 e/Å <sup>3</sup>

### Chalcostibite

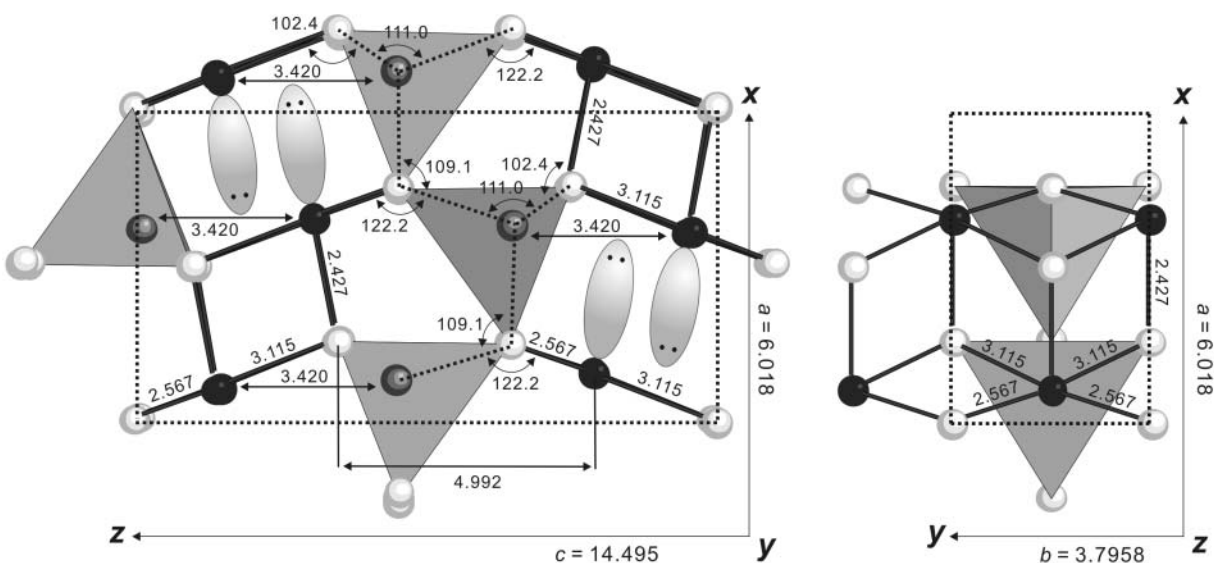


FIGURE 1. Projection of the crystal structure of chalcostibite parallel to [010] and [001] showing  $\text{CuS}_4$  tetrahedra (gray) and  $\text{SbS}_5$  square pyramid (bold stick). The white and black spheres represent S and Sb atoms, respectively. Lone-pair electrons are shown schematically. Interatomic distances and angles are given in Å and degrees, respectively.

### Emplectite

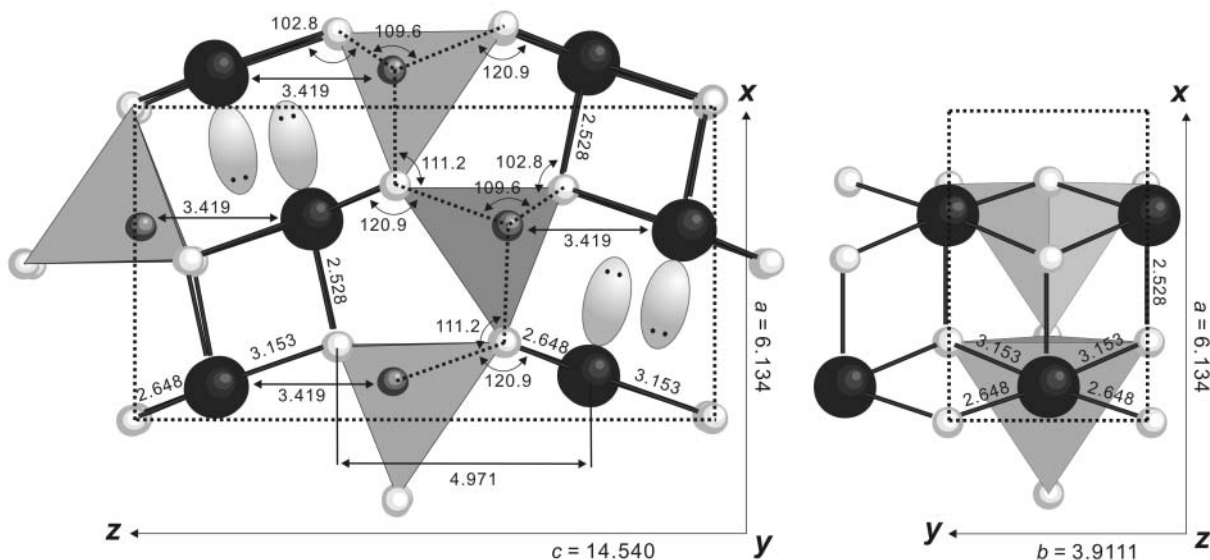


FIGURE 2. Projection of the crystal structure of emplectite parallel to [010] and [001] showing  $\text{CuS}_4$  tetrahedra (gray) and  $\text{BiS}_5$  square pyramid (bold stick). The white and black spheres represent S and Bi atoms, respectively. Lone-pair electrons are shown schematically. Interatomic distances and angles are given in Å and degrees, respectively.

effects of increasing Bi-S bond distance, caused by the larger Bi atom, and decreasing Bi-S2-Cu bond angles, caused by smaller rotation of the  $\text{CuS}_4$  tetrahedron; the latter is a consequence of the weaker stereochemical activity of the Bi  $6s^2$  lone-pair electrons

in emplectite. In summary, the anisotropic change of unit-cell parameters from chalcostibite to emplectite appears to be strongly associated with differential accommodation of lone-pair electrons associated with the pnictide metal.

**TABLE 4.** Interatomic bond distances and bond angles in chalcostibite and empectite

				Chalcostibite	Empectite
M	-S1			2.427(3) Å	2.528(7) Å
	-S2		×2	2.567(2) Å	2.648(4) Å
	-S1		×2	3.115(2) Å	3.153(5) Å
S1	-M-	S2	×2	95.9(1)°	96.6(1)°
	-M-	S1	×2	81.4(1)°	83.9(1)°
	-M-	S1		161.9(1)°	160.7(2)°
	-M-	S2		95.4(1)°	95.2(2)°
	-M-	S1	×2	169.74(8)°	170.6(1)°
	-M-	S1	×2	94.76(7)°	94.0(1)°
	-M-	S1	×2	72.3(1)°	70.9(1)°
	-M-	S1		75.06(8)°	76.7(1)°
	-M-	S1	×2	112.5(1)°	111.0(2)°
Cu	-S2			2.297(4) Å	2.303(7) Å
	-S2			2.316(4) Å	2.318(7) Å
	-S1		×2	2.331(2) Å	2.345(4) Å
	mean			2.319 Å	2.323 Å
S2	-Cu-	S2		106.8(1)°	107.3(2)°
	-Cu-	S1	×2	109.5(1)°	108.5(2)°
	-Cu-	S1	×2	111.0(1)°	109.6(2)°
	-Cu-	S1		109.0(1)°	113.0(3)°
	mean			109.5°	109.4°
M	-Cu			3.420(3) Å	3.419(5) Å
	-S1			4.992(4) Å	4.971(7) Å
Cu	-Cu		×2	3.757(3) Å	3.813(3) Å
Cu	-S2-	Cu		109.1(1)°	111.2(2)°
M	-S2-	Cu	×2	102.4(1)°	102.8(2)°
M	-S2-	Cu	×2	122.2(1)°	120.9(1)°

**ACKNOWLEDGMENTS**

We thank T. Balić-Žunić for insightful reviews of a previous version of this manuscript. The careful and thorough review and the helpful comments by an anonymous referee as well as those by P.C. Burns are gratefully acknowledged.

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MANUSCRIPT RECEIVED DECEMBER 19, 2003

MANUSCRIPT ACCEPTED AUGUST 6, 2004

MANUSCRIPT HANDLED BY PETER BURNS