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## The Crystal Structure of Wittichenite, Cu<sub>3</sub>BiS<sub>3</sub>\*

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(Received 17 April 1973; accepted 5 June 1973)

Wittichenite,  $Cu_3BiS_3$ , from the type locality in Wittichen, West Germany is orthorhombic, a = 7.723 (10), b = 10.395 (10), c = 6.716 (5) Å;  $D_{meas} = 6.01$ ,  $D_{catc} = 6.11$  g cm<sup>-3</sup>; Z = 4; space group  $P2_12_12_1$ . The structure was solved by the heavy-atom method from 695 observed symmetry-independent reflexions  $F_6^2 \ge 2\sigma F_6^2$  collected on a Picker four-circle FACS-1 diffractometer using Zr-filtered Mo Ka ( $\lambda = 0.71069$  Å) radiation. Spherical absorption corrections were applied to the data ( $\mu R = 10.5$ ) and the structure was refined by full-matrix least-squares using anisotropic temperature factors to an R value of 4.9 % ( $R_w = 6.7$  %). The structure consists of infinite BiCu\_3S\_3 chains parallel to [001] which are linked by Cu-S bonds to form continuous sheets normal to [010]. Adjacent sheets are related by the  $2_1$  axes parallel to [100] and are linked by Cu-S and Bi-S bonds. Cu is in nearly trigonal planar coordination with S (Cu-S distances 2.255 to 2.348 Å; S-Cu-S angles 110.8 to 131.8°). The packing of CuS<sub>3</sub> polyhedra in the structure wields short Cu-Cu contacts ranging from 2.61 to 2.94 Å. Bi is trigonally coordinated by S (Bi-S distances 2.569 to 2.608 Å; S-Bi-S angles 94.2 to 98.7°). S is tetrahedrally coordinated by three copper atoms and one bismuth atom.

## Introduction

Wittichenite is a bismuth sulphosalt of copper, apparently first described in 1805 by Selb (Hintze, 1904)

from Wittichen in Baden, Germany, under the name Kupferwismutherz. The original chemical analysis, which established the composition as  $Cu_3BiS_3$ , was performed by Klaproth in about 1807. Later the mineral was renamed wittichit and finally wittichenit (wittichenite) in 1853.

The early mineralogists recognized a second copper bismuth sulphosalt in the ores from Wittichen, namely

<sup>\*</sup> A report of this work was presented at the American Crystallographic Association meeting, Florida, January 1973, Paper H2.

kupferwismuthglanz, later re-named emplektit (emplectite), with composition  $\text{CuBiS}_2$ . A third name, klaprothite (or klaprotholite), thought to represent a compound of composition  $\text{Cu}_6\text{Bi}_4\text{S}_9$ , arose from investigations of the ores from the Daniel Mine in Wittichen. Detailed study (Nuffield, 1947) has shown that specimens labelled klaprothite from Wittichen are mixtures of wittichenite and empletite and examination of specimens labelled klaprothite from elsewhere have not confirmed the existence of klaprothite.

A morphological and X-ray study of a well-developed crystal of wittichenite by Nuffield (1947) established the space group as  $P2_12_12_1$  and provided the cell dimensions a=7.68, b=10.33, c=6.70 Å. Material synthesized by fusion of the elements in the course of the study gave a measured density of 6.19, compared with 6.01 measured by Frondel (Dana, 1944) on natural wittichenite labelled klaprothite, and 6.19 calculated for the cell with 4[Cu<sub>3</sub>BiS<sub>3</sub>].

Wittichenite has a metallic lustre. It breaks with a good conchoidal fracture. No cleavage has been observed. Face development is rare. The morphological habit is prismatic parallel to [001].

#### Experimental

The present study was undertaken on a specimen from the Daniel Mine in the type locality of Wittichen (Royal Ontario Museum specimen M 23304) on which a few rough, short-prismatic and heavily striated crystals of wittichenite were identified. An electron microprobe analysis of material selected from this specimen gave values which are in excellent agreement with the ideal composition,  $Cu_3BiS_3$  (Table 1).

# Table 1. Electron microprobe analysis of wittichenite from the Daniel Mine, Wittichen

		Atomic proportions				
	wt. %	Actual	Ideal			
Cu	37.79	2.98	3			
Bi	42.56	1.02	1			
S	19.13	2.99	3			
Total	<b>99</b> ∙48.					
Analyst: Elvira Gasparrini.						

Because of the irregular shape of the crystals and the high value of the linear absorption coefficient (440·2 cm<sup>-1</sup> for Mo K $\alpha$ ), it was decided to grind spheres and apply spherical absorption corrections. The crystal that was finally used for data collection had a mean diameter of 0·46 mm and was spherical to within 0·04 mm of this value. The main deviation from sphericity was between the poles which were slightly flattened due to remnant {001} faces.

Lattice parameters were calculated from a number of high- $\theta$  reflexions measured on zero-layer Weissenberg and precession films, calibrated with copper powder lines and extrapolated to  $\theta = 90^{\circ}$  against the absorption function of Nelson & Riley (1945):

a=7.723 (10), b=10.395 (10), c=6.716 (5) Å. The calculated density for the new cell dimensions and the ideal cell contents 4[Cu<sub>3</sub>BiS<sub>3</sub>], is 6.11 g cm<sup>-3</sup>.

Intensity data were collected on a Picker four-circle FACS-1 diffractometer in the  $\theta$ -2 $\theta$  scan mode up to 55° in 2 $\theta$ , using Zr-filtered Mo K $\alpha$  ( $\lambda$  = 0.71069 Å) radiation. A scan rate of 0.5° min<sup>-1</sup> with a 40 s background count on each side of the peak was used to improve the counting statistics of the weaker reflexions. Copper foil attenuators were automatically inserted into the diffracted beam whenever the counting rate exceeded 10000 c.p.s. The intensities of two standard reflexions were monitored every 40 reflexions. The variation throughout the data collection was less than 1.5%.

In total, 722 symmetry-independent reflexions were collected. The data were scaled by reference to the standard reflexions and corrected for Lorentz and polarization factors. The spherical absorption factors calculated by Weber (1969) for a  $\mu R$  value of 10.5 were applied to the data. A total of 695 intensities had  $|F^2| \ge 2\sigma |F^2|$ .

## Determination and refinement of the structure

The position of Bi was obtained from a three-dimensional Patterson map. The remainder of the structure was solved by conventional heavy-atom methods.

Structure factor calculations with the Bi position gave R = 0.39, where R is defined as:  $\sum ||F_o| - |F_c|| / \sum |F_o|$ . A subsequent  $F_o$  Fourier map revealed one Cu and the three S positions. The other two Cu positions were

Table 2.	Fractional	coordinates	and t	emperature	factors

Fractional coordinates and anisotropic thermal parameters  $\times 10^5$ ; values in parentheses are estimated standard deviations as obtained from the last cycle of least-squares refinement;

 $T = \exp\left[-\left(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl\right)\right].$ 

	x	у	Z	$\beta_{11}$	β22	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$B(Å^2)$
Bi	19716 (10)	-24401(7)	12860 (12)	230 (15)	314 (8)	856 (20)	- 20 (8)	33 (12)	- 2 (10)	1.24
Cu(1)	35179 (52)	40167 (37)	13762 (56)	852 (64)	689 (34)	1069 (74)	346 (36)	22 (60)	41 (47)	2.10
Cu(2)	19037 (84)	10470 (43)	7838 (60)	2433 (113)	720 (40)	914 (72)	590 (61)	312 (88)	234 (47)	2.75
Cu(3)	5727 (44)	46445 (35)	- 2628 (59)	403 (53)	487 (31)	1552 (82)	66 (32)	257 (60)	- 36 (43)	1.87
S(1)	-44584 (78)	24619 (57)	10918 (83)	433 (90)	364 (47)	705 (109)	8 (56) -	- 164 (82)	25 (73)	1.32
S(2)	- 31767 (82)	43669 (56)	-40779 (92)	325 (85)	338 (44)	752 (126)	52 (55)	8 (105)	- 36 (60)	1.47
S(3)	- 32136 (83)	6949 (53)	-41380 (86)	370 (87)	276 (42)	626 (120)	23 (52)	2 (100)	-78 (56)	1.49

located from a second Fourier map calculated with refined phases. Four cycles of XFLS (Ellison, 1962) isotropic least-squares refinement with all atoms in the structure-factor calculation reduced the R value to 0.08. At this stage corrections for anomalous dispersion were introduced using the values computed by Cromer (1965). Two cycles of anisotropic least-squares refinement brought the R value to 0.05. The scattering

Table 3. Comparison of observed and calculated structure factors listed as  $10F_o$  and  $10F_c$ 

Unobserved values indicated by an asterisk. Phase angles are in millicycles.

L FD FC	ALPHA	L FO FC	ALPHA	L FU FC	ALPHA	L FO FC AL	рна	L FO FC	А, РНА	L FO FC	AL PHA	L FO	FC ALPHA	L FO	FC ALPHA
H= 0, K= 0 2 1567 1669	5	H= 1, K= 0 1 910 155	329	2 799 798 3 295 292	557 155	0 442 422 1 914 870 2 264 220	564 795 304	4 351 325 5 777 722	816 816	1 243 241 2 239 192 3 153 163	470 531 686	H= 6, K=	1 005 51	4 214 5 607	52 161 90 248
4 3008 3780 6 468 429 8 1043 1020	517 491 39	2 2700 2969 3 226 213 4 404 388	524 300 9	H= 1, K= 13 0 346 355	300	3 795 782 4 341 245	259 952	H= 3, K= 11	260	H=. 4, K= 12		1 718 0 2 378 3 3 507 4	31 766 356 607 97 385	H= 7, K=	5 87 315
H=. 0, K= 1		5 192 193 6 1506 1494 7 392 349	814 34 783	1 030 605 2 300 334	224	H= 2, K= 12 3 651 802	541	1 390 398 2 1058 1073 3 292 308	246 58 367	0 68° 59 1 638 593	109 763	+ 1130 5 592 5 6 301	996 532 577 377	1 609	01 317 70 549 98 176
1 779 812 2 345 250 3 1361 1426	796 265 282	8 377 358 H= 1, K= 1	516	H= 2, K= 0	520	1 303 340 2 542 474 3 543 513	169 752 875	4 314 296	963	H= 5, K= 0	274	H=' 0, K=	2	• 250 5 012	17 687 28 829
4 993 1043 5 738 714 6 603 615	261 292 262	0 1424 181	750	1 1352 1364 2 245 249	274	1= 2, x= 13		0 670 648	783	2 1050 965 3 2213 2001	273	0 447 4	63 556 648 823	4• 7, K•	6 11 278
7 817 818 8 70* 86	794 767	2 1602 1639 3 1068 1248 4 115 76	29 421 820	4 2228 2241 5 304 296 5 385 377	814	0 594 579 1 417 384	38 361	2 455 421	19	5 884 838 6 199 195 7 766 808	795 522 782	3 1520 14	413 267 225 853	1 821 4	86 217 26 119
H= 0, K= 2	345	5 1355 1317 6 860 884 7 485 490	721	7 348 382 8 495 520	292 555	H* 3, K* U	771	0 108+ 80	160	H= 5, K= 1		6 410 4	42 010	4 170	82 463
1 336 329 2 1106 1133 3 385 395	10	B 143 169	111	H= 2, K= 1	••	2 1775 1027 3 2432 2315	23	2 91* 83 3 1581 1457	8 2 8 2	0 268 254	763	0 2247 23	s 86 527	0 292	91 789
4 2088 2172 5 919 931 6 253 229	28 516 526	0 396 381	256	1 1916 1967 2 605 598	349	5 207 196	388	5 749 702 6 70• 35	302	3 544 497 4 700 656	207	2 203 2 3 841 7	24 202 44 539 169 783	2 673 6	68 53 71 768
7 112 84 8 1035 1026	534 537	2 2437 2431 3 657 587 4 537 567	7 591 787	+ 1101 1223 > 869 858	5+2	6 100 91	49	H= 4, K= 1	147	6 1234 1208 7 72+ 140	539 653	5 381 3 6 175 1	72 712 140 641	ч 278 2 н. 7, к.	8 307
H= 0, K= 3	273	5 351 285 6 1177 1184 7 608 571	184	7 710 709	2 92 89	2 1418 1337	760	0 2393 2413 1 669 610	527 887	H+ 5, K+ 2		H+ 6, K=	•	0 195 å 1 539 å	31 791 18 808
2 1290 190 3 1534 1545	781 780	8 128 77	118	H= 2, K= 2		2 2394 2301 3 369 360	575	2 610 555 3 669 592 4 1926 1749	203	0 246 250 1 1295 1244 2 372 340	250 790 393	1 1236 11 2 295 2	96 281 49 600	3 558 5	63 691
5 661 658 6 281 287	804	0 580 612	767	1 1232 1227	762 781	4 401 380 5 909 844 5 1338 - 1271	231	5 418 400 6 484 477 7 432 424	445 584 664	3 1103 1099 4 704 55 5 1246 1161	886 310 262	3 897 8 4 442 4 5 641 5	140 783 145 622 199 792		9 85 295
8 250 234	267	2 603 647 3 2800 2811	629 750	4 830 916 5 1231 1215	605 237	8 73• 211	605	H# 4, K# 2		6 420 439 7 511 581	959 365	6 125 1 H= 6, K=	11 816 5	1 684 7 2 937 9	69 333 67 522
0 1954 2003	28	5 1213 1213 6 478 505	297	0 560 575 7 514 497 8 653 678	37 765 36	H= 3, K= 2 0 1439 1341	758	0 872 861 1 2251 2281 2 508 477	521 303 233	H= 5, K= 3 0 619 585	761	0 721 7 1 1052 10	49 62 82 720	H= 8, K= D 2376 23	0 21 526
2 101• 120 3 517 512	993 519	B 149 155	994	H# 2, K# 3		1 1574 1446 2 1668 1597 3 752 687	204 555 270	3 1077 952 4 745 679 5 788 776	741 65 835	1 640 634 2 1827 1815 3 708 690	325 568 203	2 455 4 3 444 4 4 1091 11	95 443 25 374 20 581	1 650 6 2 581 5 3 742 1	35 782 51 511 18 284
5 420 415 6 374 388	506	0 109* 29	326	0 1992 2010 1 1441 1416 2 943 959	810 423	6 690 695 5 1549 1476 6 1117 1094	40	6 109 92 7 737 796	671 283	4 277 284 5 294 287 6 1044 1021	924 19 25	5 old 5 o 340 3	76 201 57 870	• 1143 11 5 389 4	57 36 35 285
8 971 978	38	2 1152 1262	324 604	3 1698 1701 • 77• 827 5 1073 1101	258	7 570 571	787 975	H= 4, K= 3 0 2585 2744	22	7 68• 20 H• 5,K• 4	201	H= 0, K= 6 1121 11	6 95 524	H= 8,K= 6 639 7	1 Do 536
1 1195 1203	781	5 817 803 6 1053 1028	828	7 744 735 8 219 205	745 571	0 209 217	749	2 239 259 3 537 458	855 501	0 425 459 1 1309 1226	274	2 337 3 3 1216 11	43 787 41 383 62 269	1 903 8 2 298 2 3 937 9	50 320 86 756 37 770
3 1787 1811 4 524 532 5 1346 1345	217	8 232 201	488	H# 2, K# 4	4.70	2 1128 999 3 Vd1 996	985	5 121 125 6 671 665	716	2 222 216 3 1074 918 4 363 365	135	5 753 6	61 19 85 264	4 573 5 5 569 c	35 985 16 808
6 478 502 7 528 502 8 353 334	775	0 258 260	280	1 1503 1505 2 1082 1120	253	5 472 341	633	7 119 84 H- 4, K- 4	>>2	5 1153 1118 6 68* 26 7 491 471	809 888 757	H= 6, K= 0 1146 11	7 58 541	н= 8, K= 0 856 9	2 55 48
H= 0, K* 6		2 1457 1468 3 965 963	963 293 870	4 1000 1041 5 627 667	730	8 201 254	19	0 882 913 1 706 647	21	H+ 5, K= 5	•	1 142 2 263 2 3 424 4	98 15 22 678 02 845	1 368 3 2 511 5 3 362 3	71 255 29 616 82 856
0 3544 3691 1 187 147 2 167 210	519 56 493	5 1096 1116 6 549 524 7 421 420	794	7 851 676 8 609 641	322	0 1230 121a	765	3 1726 1676	297	0 645 667 1 337 339 2 1912 1898	233	4 638 5 5 321 3	91 35 03 719	+ 1278 12 5 167 2	95 537 DL 890
3 213 170	47 24	8 340 368	295	H= 2, K= 5	05	2 1452 1424	991 798	6 310 350 7 852 913	255 843 792	3 601 545 4 285 244 5 246 247	182	H= 6, K= 0 238 2	8 46 88	14 8. KF	3 96 37
6 378 343 7 305 286	992 532	0 1044 1088	763	1 2225 2244	239	5 1363 1301 6 712 713 7 502 515	270	H= 4, K= 5	6.70	ы 1057 1078 н. 5.к. 6	562	1 1065 10 2 468 4 3 872 8	75 313 48 730 82 770	1 653 6 2 224 2 3 512 5	80 802 34 435 18 329
H= 0, K= 7	107	2 1976 1968	987 795	+ 1031 956 5 1522 974	458	H= 3. K= 5	290	1 308 266 2 397 391	667 655	0 459 484 1 1561 1591	781 834	4 234 2 H1 6, K1	40 551 9	4 726 7 H= 8, K=	51 553 4
2 337 364 3 381 400 4 118 121	786 827 754	5 281 343 6 1022 1044 7 120 109	557 554 383	7 544 568	310	6 84* 80 1 733 832 2 175 1853	801 879 540	4 1143 1136 5 308 301	58	3 1452 1385	797	0 899 9	03 45 36 712	C 1405 15 1 317 3	5 534 31 954
5 218 130 6 137 146 7 809 817	74 312 289	H= 1, K+ 7		0 200+ 2087 1 630 608	25	3 375 230 4 143 140 5 772 823	703	7 224 227	730	6 337 341	62	3 352 3	35 416	2 190 1 3 423 3 4 986 9	51 635 56 164 52 29
H= 0, K= 8		0 313 331 1 820 830 2 703 706	789 744 530	2 525 665 3 727 816 4 1220 1238	214 412 543	6 1067 1051 7 303 332	21 382	0 141 54	769	0 123 38	294	0 189 1	83 565	H= 8, K=	\$
0 1545 1605 1 579 597 2 245 235	34 525 513	3 544 576 4 456 402 5 926 936	840 117 271	5 454 505 6 397 350 7 325 364	337 754 810	M= 3, K= 6	275	2 952 954 3 714 768	777 824	2 1179 1132 3 206 167	534	2 188 1	48 258	1 691 7 2 128 1	22 246 17 676
3 381 382 4 1371 1412 5 406 421	529 535 33	6 752 747 7 511 527	307	H# 2, K# 7		1 1219 1240 2 888 960 3 1497 1510	260 558 218	5 397 312 6 158 176	256 333	5 334 356 6 889 856	194 34	1 1169 10	91 783 55 562	4 612 6	04 41
6 216 212 7 69• 29	18 163	H= 1, K= 8 0 594 587	759	0 1439 1494 1 476 556 2 306 303	527 941 311	4 020 022 5 545 033 6 035 628	784 907 19	H= 4, K= 7 0 1285 1346	35	H= 5, K+ 8 D 440 425	286	3 735 7. 4 48d 4 5 935 9	26 789 61 10 89 285	0 1280 13	50 32
H= 0, K= 9 1 486 516	812	1 155 137 2 1996 2068 3 684 639	400 557 23	3 1208 1200 4 767 781 5 678 656	230 37 347	7 603 680 14 3, K# 7	788	1 523 528 2 601 563 3 462 474	377 561 696	1 894 847 2 523 493 3 624 591	218 11 305	6 603 6	80 48 1	2 127 1 3 489 5	+1 897 16 774
2 525 522 3 1194 1215 4 189 192	282 283 261	4 326 298 5 276 274 6 964 943	608 899 22	5 420 397 7 537 524	579	0 324 317 1 734 753	276 177	4 1768 1717 5 287 288 6 184 173	519 939 202	4 341 338 5 750 757	862 816	0 146 1	57 759 46 187	H* 8, K= -	7
5 506 516 6 293 267	793	н= 1, к= 9		0 16du 1099	541	2 1262 1288 3 528 554 4 502 454	29 381 616	H= 4, K= 8		н 5, к 9 0 161 198	263	2 1257 11- 3 631 5 4 183 1	48 558 59 268 39 768	1 732 7 2 389 3	5 787 30 313
0 1323 1340	532	1 1341 1362 2 564 597	228	2 282 243 3 717 711	186	5 843 833	531	0 515 505 1 1241 1296 2 744 47	794 688	1 482 490 2 1069 1061 3 323 335	982 54 580	5 658 71 6 652 61	09 814 92 21	H= 8,K= U 819 8	8
1 189 199 2 166 143 3 70* 50	498	4 308 352 5 664 671	888	5 976 954 6 293 312	533	0 769 66	89Ż	3 766 744 4 512 526 5 818 603	288	4 203 216 H# 5, K# 10	5 08	H= 7, K= 0 419 4	2 70 269	H= 9, K+	1
5 393 402	534	H= 1, K= 10	840	H= 2, K= 9		2 1155 1164	14	6 381 373 H# 4, K# 9	760	0 235 211 1 804 814	815 809	1 713 7 2 1345 12 3 662 6	13 268 63 38 09 317	2 71* 1 H= 9, K=	2 435
1 1317 1309	278	0 472 464	773	1 1137 1160 2 489 485	345	5 769 733 6 655 635	256	0 1994 1970 1 484 522	527 25	2 136 108 3 688 676	215 819	4 209 20 5 476 40 6 509 51	ol 901 84 811 51 495	D 67.	19 254
2 580 588 3 633 658 4 113 128	794 271	2 702 703 3 231 204 4 361 378	625 501	6 688 722 5 682 496	581	H+ 3, K+ 9		2 4/7 493 3 506 466 4 1063 1032	423 62 33	H= 5, K+ 11 0 366 356	271	H= 7, K=	3	4 • • • • • • • • • • • • • • • • • • •	3 16 287
э 648 687 Н= 0+ K= 12	184	у чэр зүр н= 1, к» 11	,•,	H= 2, K= 1G	-20	1 654 593 2 644 639	612 541	9 173 207	*99	2 1137 1118	569 521	0 211 2 1 1102 12 2 1524 15	62 778 51 823 20 12	1 939 9 2 372 3	0 247 10 518
0 1082 1053	36 547	0 461 479 1 787 855	786 842	0 553 581	52 716	5 508 567 4 421 389 5 620 557	195 162	0 519 519 1 241 255	529 309	H= 6, K= 0 0 1536 1368	22	3 1285 12- 4 220 1 5 552 5	40 796 99 566 74 281	H= 9, K= D 203 1	4 86 271
3 373 349	539	3 552 570 4 529 545	847 310	2 557 300 3 673 664 4 711 734	341	4* 3. K* 10	112	3 886 868 4 395 351	788 986	2 126 85 3 1213 1121	275 539 785	d= 7, K=		1 309 2 2 1257 13	2 162 6 65
1 126 137	914	H= 1, K= 12	200	н= 2, <u>к</u> = 11	143	1 962 917 2 798 791	263	H= 4, K= 11	-	• 1301 1214 5 754 740 6 284 293	525 789 505	0 197 2 1 435 4 2 702 6	55 255 86 797 70 505	H= 9, K- D 67+	3 12 15
2 303 399	241	1 355 375	47.1			2 090 090		A 040 000	24			3 301 4	00 909	\$ 74 <u>3</u> 8	28 844

factors used in these calculations were taken from Cromer & Mann (1968).

The initial weights of the structure factors were derived from the counting statistics as described by Stout & Jensen (1968). However, the standard deviation of an observation of unit weight calculated from the expression

$$S_1 = \left[\sum w \varDelta F^2 / (m-n)\right]^{1/2}$$

in which w is the weight, m the number of observations and n the number of parameters varied in the leastsquares refinement, had a value of 2.52 indicating slight errors in the assignment of the weights to the structure factors. A plot of  $\overline{\Delta F_o}/\overline{F_o} vs. 1/\overline{F_o}$  for groups of 50 reflexions was fitted by a least-squares routine to a second order polynomial from which the expression  $(0.039F_o + 1.30 + 24.37/F_o)$  was derived for  $\sigma_{Fo}$ and used in the final weighting scheme,  $w = 1/\sigma_{Fo}^2$ . Extra cycles of anisotropic refinement with new weights converged to R = 0.049 and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ = 0.067. The final value of  $S_1$  equalled 1.06.

A difference Fourier map revealed an excess electron density of about  $2 \cdot 8 \text{ e } \text{Å}^{-3}$  in the vicinity of the Bi atom, the actual centre of the atom being located at  $+1 \cdot 5$ e Å<sup>-3</sup>. The remainder of the map did not reveal any anomalies.

The atomic positional parameters and their corresponding temperature factors are listed in Table 2. The comparison of observed and calculated structure factors is given in Table 3.

An attempt to establish the absolute configuration of the structure (Ibers & Hamilton, 1964), resulted in R=0.048 for the enantiomorph. The ratio  $R_1/R_2$  is 1.02 and according to Hamilton's (1965) significance test, the value,  $\mathcal{R}_{1,632,0.01}=1.005$ , indicates that the enantiomorph can be accepted as a correct model at a 0.01 significance level. However, the result of the test should be treated with some reservation in the present case. Because Bi is a strong anomalous scatterer (Mo K $\alpha$ ,  $\Delta f' = -4.54$ ,  $i\Delta f'' = 10.65$ ), one would expect a more pronounced difference between the two R values. The explanation for the small difference must lie in the material itself. Wittichenite, like most sulphosalt minerals, has a non-uniform mosaic spread over the volume of the crystal. This is likely to produce systematic errors in the intensities of some reflexions. The configuration shown here (Table 2) is the one which corresponds to the higher R value.

## **Discussion of the structure**

Tables 4 and 5 give, respectively, the interatomic distances and angles in the wittichenite structure and their estimated standard deviations as calculated from the ORFFE (Busing, Martin & Levy, 1964) program. The

#### Table 5. Interatomic angles

Estimated standard deviation of all angles is  $0.5^{\circ}(2\sigma)$ 

Metal-atom polyhedra	Bi	$S(1^{iv})$ BiS( $2^{iv}$ ) $S(1^{iv})$ BiS( $3^{iv}$ ) $S(2^{iv})$ BiS( $3^{iv}$ )	98·7° 94·2 95·2
	Cu(1)	$S(1^{i}) - Cu(1) - S(3^{iii})$ $S(1^{i}) - Cu(1) - S(3^{iv})$	124·2 123·7
	Cu(2)	$\begin{array}{l} S(3^{iii}) \longrightarrow Cu(1) - S(3^{iv}) \\ S(1^{iii}) \longrightarrow Cu(2) - S(2^{iii}) \\ S(1^{iii}) \longrightarrow Cu(2) - S(2^{iv}) \end{array}$	111·4 131·8 116·2
	Cu(3)	$\begin{array}{l} S(2^{111}) & -Cu(2) - S(2^{1v}) \\ S(1^{111}) & -Cu(3) - S(2^{11}) \\ S(1^{111}) & -Cu(3) - S(3^{1v}) \\ S(1^{111}) & -Cu(3) - S(3^{1v}) \end{array}$	110·8 121·2 114·7
		$S(2^{n}) - Cu(3) - S(3^{n})$	124.0
Sulphur-atom polyhedra	S(1)	$\begin{array}{l} Bi^{iv} &S(1) & -Cu(1^{i}) \\ Bi^{iv} &S(1) & -Cu(2^{iii}) \\ Bi^{iv} &S(1) & -Cu(3^{11i}) \\ Cu(1^{i}) & -S(1) & -Cu(2^{1ii}) \end{array}$	115·2 90·4 101·3 83·0
		$Cu(1^{i})$ -S(1) -Cu(3 <sup>iii</sup> ) $Cu(2^{iii})$ -S(1) -Cu(3 <sup>iii</sup> )	136·3 121·5
	S(2)	$\begin{array}{c} \text{Bi}^{\text{iv}}\text{S}(2) - \text{Cu}(2^{\text{iii}}) \\ \text{Bi}^{\text{iv}}\text{S}(2) - \text{Cu}(2^{\text{iv}}) \\ \end{array}$	114·7 96·5
		$B_1^{iv} = S(2) = Cu(3^{iv})$ $Cu(2^{iii}) = S(2) = Cu(2^{iv})$ $Cu(2^{iii}) = S(2) = Cu(2^{iv})$	115.2
		$Cu(2^{iv}) -S(2) -Cu(3^{ii})$ $Cu(2^{iv}) -S(2) -Cu(3^{ii})$	80.2
	S(3)	$\operatorname{Bi}^{iv} - \operatorname{S}(3) - \operatorname{Cu}(1^{iii})$	97.8
		$Bi^{iv} = S(3) = Cu(1^{v})$ $Bi^{iv} = S(3) = Cu(3^{iv})$	86.1
		$Cu(1^{111})-S(3) - Cu(1^{1v})$	132.8
		$Cu(1^{111})-S(3) - Cu(3^{1v})$ $Cu(1^{1v}) - S(3) - Cu(3^{1v})$	72·2 68·1

## Table 4. Interatomic distances

Symmetry positions: i x, y, z; ii  $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$ ; iii  $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$ ; iv  $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$ .

Estimated standard deviations in parentheses.

		Bi	C	u(1)	С	u(2)	(	Cu(3)
Metal-atom polyhedra	S(1 <sup>iv</sup> ) S(2 <sup>iv</sup> ) S(3 <sup>iv</sup> )	2·608 (6) Å 2·569 (6) 2·600 (6)	S(1 <sup>i</sup> ) S(3 <sup>iii</sup> ) S(3 <sup>iv</sup> )	2·256 (7) Å 2·306 (7) 2·314 (7)	$S(1^{iii}) \\ S(2^{iii}) \\ S(2^{iv})$	2·257 (7) Å 2·255 (8) 2·309 (7)	S(1 <sup>111</sup> ) S(2 <sup>11</sup> ) S(3 <sup>1v</sup> )	2·259 (7) Å 2·261 (7) 2·348 (8)
	S	5(1)	S	5(2)	S	5(3)		
Sulphur-atom polyhedra	Bi <sup>iv</sup> Cu(1 <sup>i</sup> ) Cu(2 <sup>iii</sup> ) Cu(3 <sup>iii</sup> )	2·608 (6) Å 2·256 (7) 2·257 (7) 2·259 (7)	Bi <sup>iv</sup> Cu(2 <sup>iii</sup> ) Cu(2 <sup>iv</sup> ) Cu(3 <sup>ii</sup> )	2·569 (6) Å 2·255 (8) 2·309 (7) 2·261 (7)	Bi <sup>iv</sup> Cu(1 <sup>iii</sup> ) Cu(1 <sup>iv</sup> ) Cu(3 <sup>iv</sup> )	2.600 (6) Å 2.306 (7) 2.314 (7) 2.348 (8)		
Shortest metal-metal distances	Bi——E Cu(1)–C Cu(2)–C Cu(3)–C	6 <sup>111</sup> 4·232 (1 Cu(3 <sup>1</sup> ) 2·610 (5 Cu(3 <sup>111</sup> ) 2·944 (8 Cu(1 <sup>11</sup> ) 2·743 (6	) Å ) )					

Table 6.	Average Cu–S distances	and average S-Cu-S	angles in Cu–S	3 polyhedra, and	d deviations of	f the
		polyhedra from	planarit y			
verage	Average					

Average Cu–S distances 2·292 Å 2·274 2·239	Average S-Cu-S angles 119.8° 119.6 120.0	Atoms in the plane* S(1 <sup>1</sup> )†, S(3 <sup>111</sup> ), S(3 <sup>1v</sup> ) S(1 <sup>111</sup> ), S(2 <sup>111</sup> ), S(2 <sup>1v</sup> ) S(1 <sup>111</sup> ), S(2 <sup>111</sup> ), S(2 <sup>1v</sup> )	Atoms out of the plane Cu(1) 0.101 Å Cu(2) -0.150 Cu(3) 0.029	<i>A</i> 0.692 0.849 0.290	<i>B</i> - 0.552 - 0.526 0.226	C 0·465 0·058 0·929	D 4·717 1·699 - 1·157
		<ul><li>* The equation of</li><li>† The symmetry c</li></ul>	the plane is $Ax + B$ ode is the same as i	by + Cz + D = n Table 4.	0.		
	2.256	S(3 <sup>III</sup> ) 2 306 124 2 Cu(1) 123 7 S(1 <sup>I</sup> ) 2 314 S(3 <sup>IV</sup> )	Cu Cu(!')	2 257 2 256 115.2 2.608	S(1)/2 IO/3 Bi <sup>1V</sup>	Cu(3 <sup>™</sup> 259	')
	2.309 S(2	S(2 <sup>III</sup> ) 2.255 10.8 Cu(2) 131.8 Cu(2) 16.2 S(	۱''')	2.569 (S(2)) 1147 Cu(2 <sup>111</sup> )	96 5 80 2 12 261 117 0 Cut 2 255	Cu(2 <sup>IV</sup> )	
9	5(1 <sup>111</sup> ) 2:259	S(2 <sup>III</sup> ) 2 261 121 2 124 0 Cu(3) 114.7 2 348 S(	Bi <sup>IV</sup> 3 <sup>IV</sup> )	2 600 97 8 (S(3) Cu(1 <sup>IV</sup> )	Cu(1 2 306	<sup>2 348</sup> Cu(3 <sup>1v</sup> )	

Fig.1. Cu in trigonal planar coordination with S. Coordination of 3Cu and 1Bi about S.

standard deviations include the errors in cell parameters.

All Cu atoms are in nearly trigonal planar coordination with S. The Cu–S distances range from 2.255 to 2.348 Å and the S–Cu–S angles from 110.8 to 131.8° (Fig. 1). Table 6 gives the averages of these values and the offset of the Cu atom from the S plane for each of the three CuS<sub>3</sub> polyhedra. Although Cu is usually tetrahedrally coordinated by S in the ore minerals, trigonal coordination has been observed in a few structures including low-chalcite Cu<sub>2</sub>S (Evans, 1971), the unnamed PbCu<sub>4</sub>Bi<sub>5</sub>S<sub>11</sub> (Kupčík & Makovický, 1968),



Fig. 2. Bi in trigonal pyramidal coordination with S.



Fig. 3. Arrangement of Bi along [100]. Bi-Bi=4·232 Å. Bi<sup>111</sup>-S distances: S(2<sup>11</sup>) 2·569, S(3<sup>11</sup>) 2·600, S(1<sup>11</sup>) 2·608, S(3<sup>1v</sup>) 3·434, S(2<sup>1v</sup>) 3·558, S(1<sup>1v</sup>) 3·766, 3·992 Å.

and the isostructural compounds binnite  $Cu_{12}As_4S_{13}$ (Wuensch, Takéuchi & Nowacki, 1966) and tetrahedrite  $Cu_{12}Sb_4S_{13}$  (Wuensch, 1964). The Cu–S distances in the CuS<sub>3</sub> polyhedra in these minerals vary between 2.20 and 2.89 Å with an average of about 2.28 Å. The wittichenite values are, therefore, normal.

The Bi atom and its three closest S neighbours occupy the corners of a trigonal pyramid with Bi at the vertex (Fig. 2). The Bi–S bond lengths are 2.569, 2.600and 2.608 Å; the S–Bi–S angles are nearly orthogonal, ranging from 94.2 to  $98.7^{\circ}$ . More distant S neighbours occur at 3.434 Å and beyond this value (Table 7).

I	abl	le	7		Cl	osest	S	neig	h	bou	rs	to	Bi	i
-				•	∽.	00001	~	11015						

	Bi at $x = 0$	20, y = 0.76,	z = 0.13.
No.	S	<i>z*</i>	Bi–S
1	2 <sup>iv</sup>	- 0.09	2·569 ņ
2	3 <sup>iv</sup>	-0.09	2.600
3	1 <sup>i v</sup>	0.39	2.608
4	311	0.09	3.434
5	211	0.09	3.558
6	2'''	0.41	3.706
7	111	0.61	3.766
8	3111	0.41	3.891
9	111	-0.39	3.992
*	Fractional	coordinates	of S atoms.

† E.s.d. 0.006–0.007 Å.

Kohatsu & Wuensch (1971) have compared the coordination of Bi in the known bismuth ore mineral structures. Three short  $(2.7 \pm 0.15 \text{ Å})$ , nearly orthogonal Bi-S bonds may be identified in all the structures. Three or four more distant S neighbours are also present of which the fourth and fifth S atoms at distances of  $3.0 \pm 0.15$  Å usually complete a square pyramid about the Bi atom. When the fourth and fifth S atoms are taken into account, a square pyramid of S atoms about Bi can also be observed in wittichenite. However, the coordination of S about Bi in wittichenite has certain unique features. Firstly, the three nearest S atoms are closer to the Bi atom than in the other structures and secondly, the first of the more distant neighbours is at 3.43 Å, rather than at about 3.0 Å. The Bi coordination in wittichenite is, therefore, more rigorously trigonal and resembles the coordination which is characteristic for S about As and to a lesser extent about Sb, in the sulphosalts in which these semimetals prevail.

The shortest Bi-Bi contacts (4.232 Å) are in the (010) plane in which Bi is arranged in a zigzag fashion parallel to [100]. The BiS<sub>3</sub> polyhedra along such a row point in the same direction and may be pictured as loosely connected into a chain in which each Bi atom shares two of its three closest S atoms with one other Bi atom (Fig. 3). The coordinating S polyhedra have the form of trigonal prisms which are joined by sharing an edge in the basal plane. In such a prism, the Bi atom has three close and three considerably more distant S neighbours (atoms 4, 5 and 7 of Table 7) at 3.434, 3.558 and 3.766 Å.



Fig.4. Projection of the wittichenite structure on (001). Fractional coordinates are given for one chain.



Fig. 5. ORTEP plot of part of wittichenite structure showing anisotropic thermal vibrations of the atoms drawn with 50 % probability.

Each S atom coordinates one Bi and three Cu atoms (Fig. 1). The metal-S-metal angles given in Table 5 indicate a wide departure from the ideal tetrahedral bond angle of 109°28'. A comparison of the mean S-Bi and S-Cu bond lengths in wittichenite with the sums of the corresponding covalent, tetrahedral radii (Evans, 1964) shows that S-Bi distances are slightly longer and S-Cu distances slightly shorter than the sums.

	Mean S-metal	Sum of tetrahedral
	distances in	covalent radii
	wittichenite	(Evans, 1964)
S-Bi	2·59 Å	2·50 Å
S–Cu	2.29	2.39

Fig. 4 is a projection of the structure of wittichenite on (001). The most prominent and distinct structural feature is a series of infinite  $BiCu_3S_3$  chains extending parallel to [001]. Each chain is symmetrical about a central  $2_1$  axis. The chains are situated with the intermediate dimension, which is about 10.4 Å in length, parallel to (120) or (1 $\overline{2}$ 0). Parallel chains are linked by Cu–S bonds at intervals of 3.36 Å along [001] and overlap slightly to form continuous sheets normal to [010]. Adjacent sheets are related by  $2_1$  axes parallel to [100] and linked by Cu–S and Bi–S bonds. The two types of bond alternate along [100] at intervals of  $\frac{1}{2}a$  and occur at intervals of 1*c* along [001]. The unit cell contains two sheets.

The three kinds of  $Cu_3S_3$  polyhedron have distinctly different functions in the structure. The Cu(1) polyhedra form the cores of the chains and lie entirely within individual chains. Only two S atoms of each Cu(2) polyhedron lie in the same chain; the third S is in an overlapping chain and therefore the Cu(2) polyhedra link the chains into sheets. Similarly, only two S atoms of each Cu(3) polyhedron are in the same chain; the third S is in the chain of an adjacent sheet. Thus the Cu(3) polyhedra assist in binding the sheets into a three-dimensional structure.

The structure of wittichenite bears a resemblance to other sulphosalt structures that consist of frameworks of complex, essentially discrete chains (*e.g.* aikinite, PbCuBiS<sub>3</sub>), but the similarity is superficial. The wittichenite chains are basically  $Cu_3S_3$  in composition and characterized by trigonal planar coordination of S about Cu (Fig. 5). The more common coordination in sulphosalts is tetrahedral.

We wish to express our thanks to Miss Elvira Gasparrini for the electron microprobe analysis, to Dr J. Mandarino of the Royal Ontario Museum for the loan of a specimen, to Dr Klaus Dichmann for providing us with the weighting program and to the National Research Council for a grant (to E.W.N.) to support the work.

Note added in proof:- A short account of an independent solution of the structure of wittichenite has recently been given by Matzat (1972). The refinement was carried to an R value of 13.5% with isotropic temperature factors. The interatomic distances and angles are in substantial agreement with our values.

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