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The crystal structure of vrbaite $Hg_3Tl_4As_8Sb_2S_{20}$*

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Auszug

Die Kristallstruktur von Vrbait wurde bestimmt. Vier Formeleinheiten $Hg_3Tl_4As_8Sb_2S_{20}$ sind in der rhombischen Zelle, $a = 13{,}399$, $b = 23{,}389$, $c = 11{,}287$ Å, Raumgruppe $C2ca$—C_{2v}^{17}, enthalten. Die Struktur wurde mittels einer Art Superpositionsmethode auf Grund einer dreidimensionalen Pattersonfunktion gefunden; $R = 4{,}8\%$.

Die Vrbaitstruktur ist durch unendliche As_2SbS_5-Ketten parallel c und durch $Hg_3As_4S_{10}$-Schichten normal zu b charakterisiert. Die ersteren umgeben („sandwich") die Tl-Atome und bilden Schichtbereiche („slabs") normal zur b-Axe. Diese Schichtbereiche und die $Hg_3As_4S_{10}$-Schichten, welche die anderen Tl-Atome umgeben, wechseln in der b-Richtung ab. Die gefundene Struktur erklärt gut die gute Spaltbarkeit parallel (010).

Vrbait ist unseres Wissens die erste Struktur mit gemischten (As,Sb)-Ketten.

Abstract

The crystal structure of vrbaite has been determined. Four chemical units of $Hg_3Tl_4As_8Sb_2S_{20}$ are contained in the orthorhombic unit cell: $a = 13.399$, $b = 23.389$, $c = 11.287$ Å, symmetry $C2ca$—C_{2v}^{17}. The structure was solved through a kind of superposition method using the three-dimensional Patterson function. The final discrepancy index R is 4.8%.

The structure of vrbaite is characterized by infinite As_2SbS_5 chains parallel to c and by $Hg_3As_4S_{10}$ sheets perpendicular to b. The former sandwich the Tl atoms and make slabs perpendicular to the b axis. These slabs and the $Hg_3As_4S_{10}$ sheets, sandwiching the other Tl atoms, are arranged alternately along the b direction. The good cleavage parallel to (010) can be well explained by the structure. Vrbaite is the first structure with mixed (As,Sb) chains.

Introduction

Vrbaite is a very rare sulfosalt, found by JEŽEK (1912) in a specimen from Allchar, Macedonia. JEŽEK made morphological studies and

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described its point symmetry as $2/m\ 2/m\ 2/m$. KŘEHLÍK (1912) made a chemical analysis of this material and showed its formula to be $TlAs_2SbS_5$. The cell dimensions of vrbaite were determined by FRONDEL (1941). He proposed *Cmca* as the probable space group, taking account of x-ray and morphological data. Recently CAYE, PICOT, PIERROT and PERMINGEAT (1967) reexamined the chemical composition of vrbaite with the aid of electron-probe microanalysis, and obtained a new formula, $Hg_3Tl_4As_8Sb_2S_{20}$. This formula was confirmed by NOWACKI (1968).

The present investigation was undertaken to elucidate the coordinations of the sulfur atoms around the thallium atoms which show a quite irregular feature in the structures of sulfosalts, and to examine whether the antimony atoms and the arsenic atoms are in an ordered state or not.

Experimental

A specimen from Allchar, Macedonia (Naturhistorisches Museum, Wien), half of which was being used for chemical analysis (NOWACKI, 1968), was used for the present studies. A spherical crystal with radius 0.106 mm was prepared by BOND's (1951) method for the determination of the cell dimensions and intensities. The lattice constants were obtained from back-reflection Weissenberg photographs calibrated by powder patterns of silicon. A least-squares best fit of the lattice parameters was calculated with the aid of an IBM-1620 program written by N. D. JONES (unpublished). The results agree well with the values obtained by FRONDEL (1941).

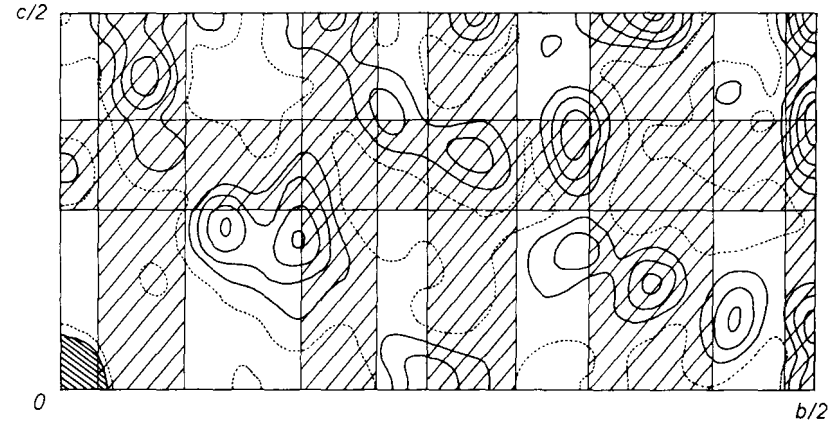
Present determination	FRONDEL[1]
$a = 13.399 \pm 0.001$ Å	13.38 ± 0.05 Å
$b = 23.389 \pm 0.001$	23.37 ± 0.05
$c = 11.287 \pm 0.001$	11.25 ± 0.05

The number of formula units, four, was calculated from the cell dimensions obtained and the measured specific gravity, 5.30 (PALACHE, BERMAN and FRONDEL, 1944).

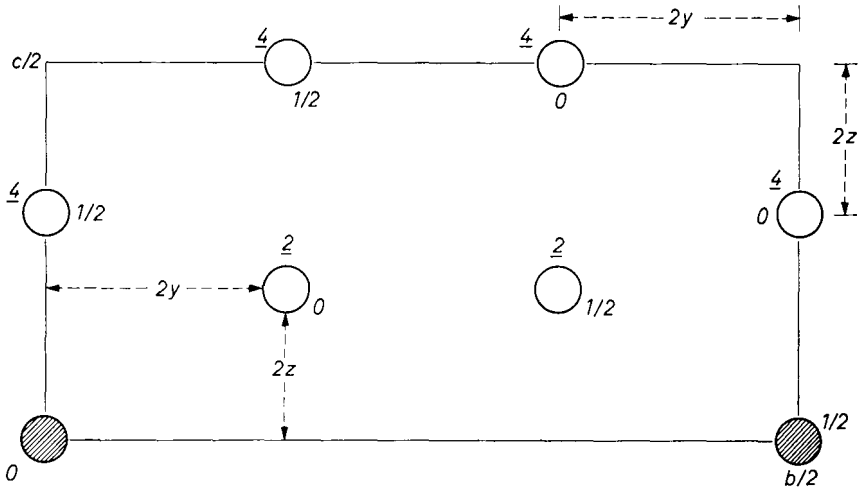
The diffraction symbol for vrbaite is $mmmC_*ca$, which permits *Cmca* and $C2ca$ as possible space groups. Since a piezoelectric test showed an acentric feature, $C2ca$—C_{2v}^{17} was selected as the correct space group.

[1] FRONDEL's values are converted to Ångstrom from kX units.

Three-dimensional intensity data (1772 independent reflections) were collected by an automated Weissenberg counter-diffractometer (Supper-Pace) using Cu$K\alpha$ radiation. One hundred and twenty-four of these reflections [with $I < 2.33\ \sigma\ (I)$] were assigned to unobserved reflections.



(*a*)



(*b*)

Fig. 1. (*a*) Patterson section $P(0,v,w)$. Rotation peaks should not exist in the shaded area. Contours are equal but in arbitrary intervals. (*b*) The vector set for equipoints 8*b*. The underlined values indicate weights of points

Determination of the structure and refinement

The Patterson function $P(u,v,w)$, evaluated with the three-dimensional data, showed that all peaks are distributed on the sections $u = n/8$ ($n = 0$, 1 and 2). All heavy peaks which correspond to the vectors between heavy atoms[2] are on the sections $u = 0$ and $1/4$. These features of the diagram suggest that all atoms are arranged nearly on planes at intervals of $1/8$ along the a direction, and all heavy atoms on every other plane. The only equipoints of the space group $C2ca$ are $4a$ (on twofold axes) and $8b$ (points in the general position)[3].

Since there are twelve mercury atoms in the cell and since this number is not divisible by eight, at least four mercury atoms should occupy the special positions. A possibility of statistical distribution of mercury atoms was omitted, because no anomaly of background intensities was observed on the films. As the space group $C2ca$ has no symmetry element to fix the x coordinate of points, the origin of the cell can be set at one mercury atom of $4a$ and the positions of at least three heavy atoms (one Hg and two Tl atoms) must be found.

The vector set of equipoint $8b$ is illustrated in Fig. 1*b*. These relations of equipoints and the heights of peaks which are expected for the vectors between heavy atoms, limit the probable positions of rotation peaks in the Patterson diagram $P(0,v,w)$, Fig. 1*a*. It was, however, impossible to find uniquely the rotation peaks of heavy atoms and another attempt was made to obtain the heavy-atom positions, because almost all peaks of the Patterson maps have broadened shapes and overlap each other.

If one component atom of a structure occupies the origin of the cell, the Patterson diagram contains the image of the true structure and the origin of the diagram coincides with that of the cell. If this crystal has axial symmetry, the image of the structure, being concentrated in one section, will also be obtained from the Harker section (the implication diagram). Therefore when we superpose the implication diagram on each section of the Patterson diagram in such a way that the origin of the former coincides with one of the symmetry axes in the cell, and when we note the peaks common in both diagrams, the image of the true structure should be found in the resultant map. In the present case, the Patterson section $P(0,v,w)$, which was drawn on a scale of one

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[2] The word "heavy atoms" will be used for mercury and thallium atoms hereafter, because the difference of their atomic scattering factors is quite small.

[3] $(0,0,0;\ \frac{1}{2},\frac{1}{2},0) + 8b$: x, y, z; $x,\bar{y},\bar{z}$; $x,\frac{1}{2}+y,\frac{1}{2}-z$; $x,\frac{1}{2}-y,\frac{1}{2}+z$.
$4a$: $x,0,0$; $x,\frac{1}{2},\frac{1}{2}$.

to two, was superposed on $P(0,v,w)$ and $P(\frac{1}{4},v,w)$. The result, however, showed still too many candidates for the heavy atom positions.

In order to eliminate some of the candidates, the relations of the cross vectors between the origin and the points in the general positions were derived. The end points of vectors show special relations as indicated in Fig. 2: these points are related to each other by three twofold axes. One of them designated as I is a component of the symmetry elements in the Patterson space group *Cmmm*, while the others, II and III, being equivalent, are additional ones. When two sets of Patterson diagrams are superposed according to the additional operations, the cross vector peaks between the atom of the origin and the atoms of the general positions can be obtained. This result also includes the image of the actual structure.

The above procedure eliminated most of the peaks in the Patterson section. The implication diagram was also superposed on the resultant maps, and five peaks common in both diagrams were adopted as candidates (Figs. 3*a* and 3*b*). In order to eliminate the number of candidates and to obtain the relative positions of each of the heavy atoms, five sets of minimum functions were evaluated using the origin atom, each of the candidates and their symmetrically equivalent positions. Four minimum-function diagrams drawn with four points I, II, III and IV (Figs. 3*a* and 3*b*) were compatible with each other, and these peaks were considered to correspond to one mercury, two thallium and one antimony atoms. Position I was regarded as the antimony atom, because the peak height in the minimum-function diagram is lower. The relative positions of these peaks, having been impossible to derive by the operation in Fig. 2, are found from minimum-function diagrams. The structure factors were calculated with the coordinates obtained for the reflections which are in the range of $\sin\theta \leq 0.7$. The discrepancy index R was about 43%. The atomic scattering factor of mercury was used for both mercury and thallium atoms at this stage. The remaining atoms were found by successive three-dimensional Fourier and difference Fourier syntheses. In the course of this procedure, the antimony atom and one of three heavy atoms (denoted II in Fig. 3*a*) revealed an anomaly in the difference map; that is, a deep depression was found at the position of the latter and an elevation at the position of the former. Besides, the coordination of sulfur atoms around them was quite strange: atom I, which was regarded as Sb, has two nearest sulfur atoms and the coordination of atom II was a flat trigonal pyramid. Therefore the Sb atom (I) and atom II were

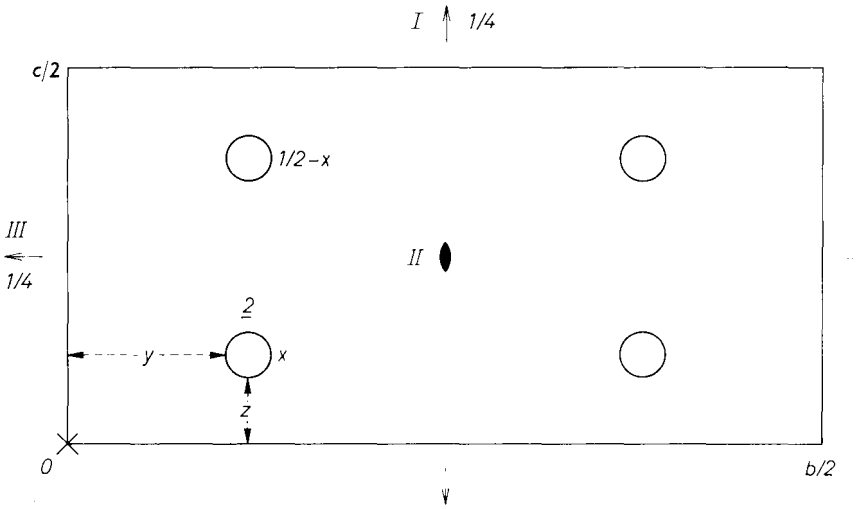

Fig.2. The relations of cross vectors between the origin and the points in the general positions. The underlined values indicate weights of points. I, II and III are directions of the three twofold axes

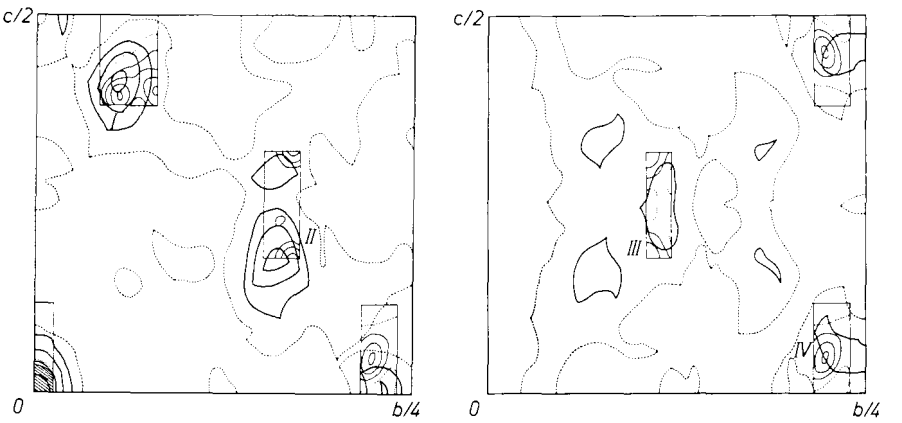

Fig. 3. Candidates for heavy atoms. The same diagram as in Fig. 1*a* was used as the implication diagram. All candidates should be in the area within the rectangular sections. (*a*) $x = 0$. (*b*) $x = 0.24 \approx \frac{1}{4}$. Independent candidates in this section are only III and IV

interchanged in position. Four arsenic and ten sulfur atoms were found in the further process. The R index was about 22% at this stage and no anomaly was found in the three-dimensional difference synthesis. The mercury atom was distinguished from thallium atoms by the difference in the coordinations around them.

Table 1. *Comparison of observed and calculated structure factors for vrbaite*

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
0	2	0	28*	79	0	8	7	123	120	1	21	3	210	216	1	5	12	179	178	2	12	6	307	317
	4		338	289		10		118	134		23		275	275		7		150	150		14		67*	57
	6		259	267		12		80	88		25		32*	44		9		104	105		16		88	74
	8		163	164		14		225	226		27		214	220		11		81	73		18		315	312
	10		160	155		16		416	441	1	1	4	865	943		13		78	78		20		103	99
	12		259	243		18		75	73		3		404	418	1	1	13	86	89		22		298	307
	14		271	283		20		122	129		5		283	294		3		62	56		24		39	25
	16		244	269		22		18*	4		7		656	711		5		22*	12	2	2	7	586	623
	18		1152	1229		24		314	330		9		295	310		7		193	186		4		166	160
	20		663	669	0	0	8	297	324		11		538	557		9		147	143		6		335	346
	22		93	54		2		268	285		13		278	281	2	0	0	402	170		8		194	210
	24		115	97		4		194	214		15		99	81		2		248	210		10		261	266
	26		355	352		6		347	371		17		407	400		4		245	228		12		147	148
	28		441	459		8		112.	118		19		387	387		6		1110	1219		14		343	342
0	2	1	116	32		10		264	297		21		305	300		8		762	795		16		63	61
	4		378	376		12		52*	43		23		72	62		10		95*	76		18		146	142
	6		450	489		14		55*	25		25		255	262		12		536	539		20		121	112
	8		831	918		16		31*	12		27		205	219		14		797	822		22		83	69
	10		587	637		18		290	298	1	1	5	723	764		16		117	129		24		22*	26
	12		705	762		20		194	198		3		241	244		18		384	386	2	0	8	263	262
	14		174	191		22		45	41		5		247	258		20		605	614		2		421	417
	16		285	298	0	2	9	49*	25		7		299	300		22		216	216		4		286	276
	18		171	168		4		361	389		9		457	483		24		308	300		6		69	49
	20		32*	8		6		264	287		11		123	121		26		198	202		8		529	558
	22		131	139		8		292	318		13		235	248		28		78	71		10		474	508
	24		105	110		10		180	191		15		109	101	2	2	1	573	551		12		58*	35
	26		257	256		12		426	451		17		450	467		4		64*	82		14		165	157
	28		14*	10		14		67	66		19		373	378		6		464	483		16		97	91
0	0	2	344	389		16		33*	37		21		260	266		8		49*	53		18		61	20
	2		196	193		18		123	123		23		200	200		10		136	100		20		166	169
	4		928	1046		20		53	54		25		180	185		12		132	100		22		150	152
	6		234	271	0	0	10	667	699	1	1	6	241	255		14		464	476	2	2	9	352	349
	8		717	781		2		249	254		3		454	476		16		551	556		4		126	139
	10		114*	82		4		43*	27		5		351	373		18		113	81		6		239	241
	12		152	171		6		200	203		7		239	237		20		382	388		8		120	114
	14		453	475		8		186	193		9		56*	55		22		89	80		10		184	194
	16		49*	27		10		61	74		11		339	341		24		316	315		12		201	197
	18		93	50		12		65	67		13		147	154		26		131	131		14		97	105
	20		175	181		14		56	52		15		445	451		28		182	193		16		240	248
	22		500	514		16		96	99		17		249	252	2	0	2	372	372		18		173	166
	24		69	9		18		194	201		19		82	76		2		841	884		20		187	189
	26		255	255	0	2	11	24*	1		21		193	206		4		273	267	2	0	10	267	255
	28		150	149		4		206	213		23		259	256		6		122*	93		2		422	423
0	2	3	366	378		6		58	54		25		97	107		8		196	194		4		314	317
	4		1360	1640		8		324	334	1	1	7	395	417		10		754	780		6		282	295
	6		178	172		10		60	53		3		440	456		12		252	255		8		68	64
	8		621	678		12		336	352		5		499	528		14		237	206		10		288	287
	10		298	322		14		387	389		7		414	439		16		674	704		12		187	182
	12		87*	85		16		141	142		9		124	142		18		257	260		14		301	305
	14		822	881	0	0	12	166	162		11		296	312		20		254	250		16		212	207
	16		489	495		2		243	239		13		425	442		22		236	234		18		64	52
	18		20*	9		4		297	297		15		395	399		24		115	110	2	2	11	106	96
	20		235	238		6		61	52		17		320	320		26		88	89		4		163	164
	22		253	251		8		36	9		19		179	167		28		223	228		6		703	714
	24		450	461		10		33	13		21		263	272	2	2	3	369	365		8		173	171
	26		68	69		12		41	15		23		120	119		4		305	303		10		36*	42
	28		27*	8		14		111	111	1	1	8	207	212		6		199	176		12		286	291
0	0	4	242	255	0	2	13	61	59		3		257	268		8		200	204		14		178	179
	2		24*	59		4		203	216		5		399	428		10		200	206		16		74	78
	4		687	766		6		63	65		7		190	195		12		663	684	2	0	12	243	228
	6		353	388		8		107	111		9		99	91		14		312	302		2		193	193
	8		823	919		10		204	209		11		148	144		16		138	130		4		101	92
	10		327	356	1	1	1	98*	136		13		151	164		18		541	548		6		105	109
	12		672	713		3		116*	104		15		174	170		20		313	308		8		54	49
	14		37*	11		5		388	404		17		128	147		22		73	62		10		193	187
	16		214	227		7		835	909		19		155	156		24		326	330		12		153	161
	18		173	166		9		701	738		21		185	187		26		248	257	2	2	13	436	427
	20		238	253		11		526	543		23		155	158	2	0	4	89	89		4		110	110
	22		89	80		13		526	552	1	1	9	358	365		2		492	514		6		149	149
	24		86	92		15		253	257		3		241	242		4		250	231		8		47	51
	26		226	240		17		139	121		5		154	166		6		412	422	3	1	1	171	157
0	2	5	109	119		19		260	261		7		193	203		8		113	116		3		237	222
	4		276	302		21		182	188		9		264	281		10		553	567		5		688	688
	6		32*	68		23		260	254		11		301	312		12		520	534		7		649	649
	8		521	577		25		255	254		13		248	256		14		215	206		9		676	676
	10		540	583		27		141	143		15		302	302		16		62*	49		11		551	536
	12		96	88	1	1	2	155	127		17		172	164		18		199	186		13		651	651
	14		306	330		3		519	546		19		324	322		20		159	155		15		138	104
	16		86	98		5		600	638		21		76	79		22		385	385		17		308	303
	18		170	170		7		166	185	1	1	10	96	98		24		93	102		19		39*	70
	20		390	398		9		41*	58		3		310	310		26		23*	20		21		100	74
	22		7*	20		11		190	205		5		114	110	2	2	5	362	369		23		213	213
	24		49	45		13		396	402		7		214	217		4		104	101		25		229	226
	26		138	142		15		305	297		9		45*	38		6		517	548		27		213	219
0	0	6	594	633		17		122	131		11		307	306		8		232	245	3	1	2	267	275
	2		182	196		19		176	171		13		33*	23		10		95	85		3		784	792
	4		25*	7		21		281	283		15		85	91		12		431	444		5		831	842
	6		482	524		23		156	163		17		151	150		14		196	185		7		174	147
	8		682	780		25		190	196		19		127	120		16		348	357		9		181	192
	10		537	595		27		166	171	1	1	11	46*	19		18		92	85		11		147	151
	12		814	899	1	1	3	494	511		3		181	177		20		197	193		13		424	430
	14		61*	80		3		460	499		5		143	144		22		127	131		15		319	310
	16		143	154		5		297	306		7		136	127		24		40*	39		17		147	133
	18		126	118		7		145	160		9		229	232		26		45	43		19		121	122
	20		92	99		9		673	726		11		126	127	2	0	6	98	89		21		316	305
	22		106	107		11		325	348		13		145	155		2		98	92		23		260	257
	24		213	222		13		157	169		15		71	68		4		347	363		25		246	245
0	2	7	84	70		15		187	200		17		57	46		6		103	43		27		203	208
	4		663	743		17		272	271	1	1	12	157	152		8		557	574	3	1	3	219	202
	6		105	76		19		180	170		3		229	234		10		55*	25		3		684	681

Table 1. *(Continued)*

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
3	5	3	141	125	3	9	11	242	249	4	10	6	439	434	5	9	3	445	428	5	9	12	38*	45
	7		206	199		11		178	170		12		353	351		11		389	374		11		101	97
	9		492	479		13		158	157		14		59*	32		13		118	134	5	1	13	98	97
	11		488	487		15		158	150		16		96	91		15		386	370		3		95	88
	13		125	116	3	1	12	150	139		18		277	272		17		299	275	6	0	0	111*	98
	15		410	398		3		87	92		20		233	237		19		114	90		2		347	302
	17		368	356		5		49	48		22		120	123		21		272	267		4		220	203
	19		39*	34		7		52	43		24		100	99		23		208	196		6		940	910
	21		291	291		9		34	43	4	2	7	210	221		25		99	92		8		738	707
	23		283	271		11		80	74		4		420	411	5	1		521	512		10		76*	63
	25		82	76		13		80	73		6		155	144		3		340	341		12		346	318
	27		162	159	3	1	13	61	63		8		156	148		5		278	255		14		734	699
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	3		494	504		5		21*	15		12		363	351		9		153	153		18		415	390
	5		260	247		7		263	254		14		47*	28		11		543	520		20		570	552
	7		591	583	4	0	0	2102	2420		16		701	706		13		180	160		22		191	190
	9		160	151		2		118*	103		18		143	138		15		169	165		24		263	255
	11		592	586		4		72*	66		20		81	75		17		298	283		26		251	255
	13		210	199		6		380	364		22		61	62		19		349	338	6	2	1	415	392
	15		117	102		8		308	299	4	0	8	150	145		21		235	232		4		161	114
	17		418	402		10		320	313		2		260	251		23		66	61		6		435	414
	19		297	291		12		1065	1039		4		287	283		25		270	274		8		133	121
	21		293	286		14		150	134		6		402	403	5	1	5	573	544		10		111	55
	23		84	79		16		409	404		8		235	218		3		322	321		12		59*	47
	25		246	248		18		907	895		10		316	312		5		414	418		14		366	349
	27		98	104		20		467	438		12		62	42		7		301	294		16		457	427
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	5		486	484		26		147	145		18		141	133		13		235	225		22		28*	40
	7		346	350	4	2	1	154	149		20		208	205		15		316	299		24		256	241
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	15		217	222		10		751	727		6		194	195		23		271	271		4		137	133
	17		381	384		12		428	416		8		579	584		25		188	186		6		157	152
	19		365	368		14		51*	29		10		341	328	5	1	6	208	216		8		233	215
	21		295	300		16		0*	29		12		372	368		3		581	567		10		715	681
	23		254	255		18		288	279		14		53	37		5		398	394		12		260	247
	25		179	178		20		196	189		16		6*	13		7		203	188		14		185	156
3	1	6	251	254		22		54*	52		18		222	217		9		146	134		16		702	672
	3		601	600		24		267	263		20		185	180		11		303	295		18		251	231
	5		482	489		26		197	197	4	0	10	492	469		13		169	156		20		227	219
	7		128	124	4	0	2	183	177		2		252	239		15		419	411		22		160	167
	9		159	167		2		205	187		4		84	22		17		187	182		24		64	63
	11		188	204		4		1626	1778		6		250	245		19		87	74		26		85	87
	13		136	126		6		214	209		8		258	239		21		163	163	6	2	3	373	351
	15		346	337		8		249	244		10		74	69		23		264	262		4		260	258
	17		262	262		10		50*	30		12		182	174	5	1	7	324	325		6		222	172
	19		40*	17		12		104	99		14		48	59		3		483	473		8		197	190
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	23		326	327		16		513	489		18		184	190		7		393	377		12		651	611
	25		35	23		18		191	182	4	2	11	134	120		9		91	80		14		219	208
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	3		468	476		22		606	596		6		79	71		13		350	345		18		537	517
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	7		466	462		26		51	42		10		41	40		17		259	251		22		27*	31
	9		100	92	4	2	3	273	261		12		291	292		19		254	253		24		289	287
	11		221	217		4		1506	1565		14		297	290		21		276	277	6	0	4	70*	75
	13		444	443		6		120	105	4	0	12	30*	21		23		157	161		2		458	453
	15		452	451		8		465	427		2		200	189	5	1	8	180	189		4		283	275
	17		296	291		10		211	208		4		170	160		3		135	118		6		294	284
	19		224	231		12		178	115		6		42	32		5		253	243		8		168	159
	21		301	305		14		888	830		8		135	129		7		197	189		10		450	430
	23		124	127		16		487	472		10		66	60		9		11*	35		12		448	420
3	1	8	241	222		18		85*	64		12		124	116		11		276	261		14		201	181
	3		199	196		20		94	96	4	2	13	50	47		13		250	238		16		68*	78
	5		372	368		22		281	270		4		367	353		15		174	169		18		136	131
	7		241	248		24		441	439		6		52	47		17		16*	29		20		140	134
	9		51*	54		26		88	85	5	1	1	156	143		19		157	153		22		394	385
	11		205	199	4	0	4	225	206		3		82*	100		21		100	103		24		65	69
	13		312	312		2		100*	101		5		596	586	5	1	9	395	379	6	2	5	223	214
	15		214	220		4		236	225		7		628	601		3		140	130		4		64*	41
	17		69	51		6		408	397		9		544	523		5		207	210		6		518	520
	19		162	156		8		1022	1033		11		395	381		7		79	82		8		236	226
	21		104	96		10		363	335		13		526	495		9		336	330		10		172	150
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	3		40*	43		14		60*	76		17		206	201		13		228	222		14		128	115
	5		197	185		16		157	134		19		161	156		15		198	199		16		346	335
	7		157	157		18		209	200		21		47*	37		17		168	158		18		103	93
	9		350	343		20		293	287		23		140	136		19		310	307		20		149	150
	11		90	77		22		78	61		25		223	227	5	1	10	239	227		22		156	151
	13		280	272		24		29*	20		27		214	223		3		204	195		24		39	32
	15		132	139		26		309	325	5	1	2	227	227		5		164	153	6	0	6	96	90
	17		144	141	4	2	5	32*	19		3		551	543		7		227	236		2		137	129
	19		259	256		4		393	388		5		604	593		9		138	143		4		283	277
	21		74	67		6		123	30		7		69*	52		11		320	308		6		74	69
3	1	10	309	300		8		229	223		9		197	196		13		143	137		8		488	476
	3		257	254		10		387	370		11		249	239		15		118	118		10		97	65
	5		51	62		12		0*	16		13		285	272		17		136	140		12		212	217
	7		227	219		14		307	310		15		270	256	5	1	11	97	87		14		84	77
	9		176	178		16		30*	34		17		107	94		3		190	183		16		75	62
	11		320	305		18		64*	52		19		128	133		5		66	71		18		253	243
	13		164	169		20		152	147		21		223	220		7		178	169		20		114	107
	15		125	130		22		66	59		23		194	188		9		204	201		22		259	257
	17		174	177		24		70	70		25		154	153		11		119	120	6	2	7	410	406
	19		172	170	4	0	6	1386	1394		27		203	208		13		103	105		4		136	128
3	1	11	134	97		2		164	164	5	1	3	158	147	5	1	12	198	185		6		302	302
	3		193	182		4		196	200		3		634	622		3		88	89		8		149	141
	5		42	54		6		473	467		5		251	232		5		120	123		10		276	264
	7		208	209		8		450	446		7		248	241		7		88	79		12		100	91

Table 1. *(Continued)*

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
6	14	7	441	430
	16		93	73
	18		112	111
	20		133	128
	22		68	65
6	0	8	264	252
	2		393	386
	4		334	322
	6		81	75
	8		539	534
	10		453	445
	12		45*	33
	14		159	152
	16		65	47
	18		26*	24
	20		152	148
6	2	9	449	406
	4		172	168
	6		250	240
	8		121	127
	10		99	89
	12		159	152
	14		102	100
	16		214	211
	18		80	73
6	0	10	229	214
	2		387	371
	4		317	300
	6		279	273
	8		60	56
	10		256	254
	12		146	135
	14		271	267
	16		173	169
6	2	11	61	64
	4		159	147
	6		615	599
	8		161	156
	10		97	94
	12		237	228
6	0	12	165	159
	2		185	176
	4		79	72
	6		70	70
	8		29*	36
7	1	1	288	292
	3		123	86
	5		435	402
	7		857	823
	9		673	630
	11		515	468
	13		495	456
	15		129	116
	17		176	166
	19		228	210
	21		214	207
	23		175	179
	25		226	234
7	1	2	43*	73
	3		483	488
	5		631	608
	7		267	252
	9		66*	26
	11		114	101
	13		468	435
	15		300	272
	17		168	156
	19		168	157
	21		255	248
	23		181	193
	25		236	248
7	1	3	339	322
	3		425	419
	5		283	277
	7		180	169
	9		656	586
	11		173	169
	13		230	207
	15		230	222
	17		339	326
	19		108	101
	21		180	175
	23		193	191
	25		58	58
7	1	4	789	799
	3		492	495
	5		197	187
	7		530	505
	9		335	314
	11		408	374
	13		335	307
	15		123	110
	17		456	431
	19		327	322
	21		289	282
	23		58	43
7	1	5	603	611
	3		224	227
	5		264	269
	7		155	145
	9		547	521
	11		95	78
	13		197	192
	15		187	188
	17		429	412
	19		365	371
	21		274	278
	23		142	145
7	1	6	220	229
	3		424	424
	5		228	223
	7		170	158
	9		79	37
	11		214	201
	13		91	90
	15		289	279
	17		247	240
	19		77	74
	21		217	225
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	5		433	427
	7		326	317
	9		209	192
	11		275	261
	13		450	437
	15		369	362
	17		343	337
	19		109	113
	21		208	209
7	1	8	201	184
	3		265	263
	5		471	462
	7		32*	18
	9		36*	30
	11		48*	11
	13		231	229
	15		181	174
	17		179	174
	19		195	186
7	1	9	200	197
	3		132	137
	5		174	184
	7		255	250
	9		225	217
	11		334	319
	13		259	255
	15		251	247
	17		202	196
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	3		245	250
	5		86	81
	7		171	179
	9		49	51
	11		267	260
	13		32	34
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	3		129	138
	5		109	119
	7		176	178
	9		218	217
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	4		323	306
	6		163	148
	8		81*	76
	10		157	135
	12		328	305
	14		276	258
	16		348	334
	18		975	938
	20		555	537
	22		74	83
	24		86	83
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	4		320	310
	6		315	297
	8		695	625
	10		467	433
	12		552	530
	14		126	134
	16		262	245
	18		127	131
	20		69	68
	22		114	114
8	0	2	292	280
	2		153	159
	4		765	745
	6		221	232
	8		527	507
	10		223	199
	12		108	88
	14		380	355
	16		72	32
	18		129	108
	20		159	151
	22		390	390
	24		13*	11
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8	4	3	1147	1142
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	8		543	506
	10		276	257
	12		90	105
	14		701	650
	16		408	382
	18		52*	4
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	22		197	197
	24		377	381
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	8		721	691
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	12		557	525
	14		27*	27
	16		176	171
	18		167	154
	20		213	218
	22		57	59
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	4		260	255
	6		84	48
	8		419	406
	10		422	416
	12		90	72
	14		285	272
	16		55*	75
	18		158	160
	20		305	305
	22		27*	28
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	2		164	161
	4		62*	51
	6		450	437
	8		630	614
	10		477	455
	12		722	697
	14		61	80
	16		92	98
	18		109	96
	20		79	82
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	6		88	69
	8		152	110
	10		128	129
	12		74	77
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	16		351	352
	18		59	65
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	4		161	162
	6		319	310
	8		88	76
	10		248	246
	12		38*	40
	14		47*	53
	16		24*	22
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	4		308	310
	6		231	219
	8		252	254
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	4		49	51
	6		170	174
	8		161	158
	10		84	79
	12		58	59
8	2	11	74	72
	4		155	159
	6		37	40
	8		244	242
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	3		132	107
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	7		445	423
	9		493	458
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	13		394	366
	15		274	262
	17		49*	56
	19		198	186
	21		94	92
	23		242	249
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	3		290	267
	5		351	341
	7		56*	55
	9		76*	79
9	11	2	257	231
	13		198	188
	15		200	184
	17		97	107
	19		123	134
	21		185	185
	23		104	110
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	5		127	102
	7		132	122
	9		446	410
	11		361	327
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	15		164	161
	17		167	158
	19		175	173
	21		173	173
	23		224	228
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	13		161	155
	15		90	84
	17		195	190
	19		271	275
	21		197	202
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	3		173	172
	5		133	136
	7		273	272
	9		245	236
	11		251	250
	13		187	176
	15		142	136
	17		292	295
	19		236	247
	21		153	155
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	3		284	299
	5		301	307
	7		161	150
	9		49*	48
	11		274	273
	13		115	110
	15		375	375
	17		143	142
	19		41	38
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	3		312	323
	5		311	318
	7		331	329
	9		108	98
	11		209	209
	13		239	235
	15		290	282
	17		212	208
9	1	8	97	100
	3		138	138
	5		220	222
	7		230	228
	9		121	128
	11		215	212
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	3		232	235
	5		111	113
	7		74	82
	9		198	194
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	13		144	143
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	3		223	226
	5		134	133
	7		159	169
	9		60	68
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	3		379	322
	5		161	118
	7		218	215
	9		756	720
	11		479	448
	13		47*	28
	15		403	374
	17		575	559
	19		214	202
	21		189	193
	23		467	463
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	4		151	150
	6		223	235
	8		136	125
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	12		162	143
10	14	1	376	355
	16		420	405
	18		109	118
	20		205	205
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	2		507	510
	4		224	227
	6		67*	78
	8		65*	42
	10		459	439
	12		140	113
	14		124	109
	16		437	427
	18		238	227
	20		207	205
	22		223	234
10	2	3	162	168
	4		220	219
	6		125	87
	8		108	98
	10		128	127
	12		502	474
	14		235	228
	16		148	140
	18		344	341
	20		212	211
10	0	4	133	135
	2		328	331
	4		114	104
	6		327	314
	8		120	104
	10		370	352
	12		430	408
	14		141	126
	16		0*	33
	18		165	161
	20		101	98
10	2	5	271	283
	4		117	114
	6		337	335
	8		150	137
	10		85	54
	12		277	275
	14		157	158
	16		217	230
	18		74	77
	20		146	151
10	0	6	137	142
	2		0*	23
	4		235	264
	6		58*	43
	8		461	454
	10		55*	15
	12		310	309
	14		51	35
	16		100	105
	18		243	245
10	2	7	473	488
	4		157	156
	6		226	235
	8		173	176
	10		178	167
	12		124	122
	14		125	121
	16		52	50
10	0	8	165	161
	2		265	266
	4		155	151
	6		87	84
	8		354	342
	10		356	361
	12		58	52
	14		128	129
10	2	9	152	153
	4		144	140
	6		119	114
	8		45	45
	10		191	190
	12		186	190
10	0	10	251	256
	2		260	271
	4		224	227
	6		175	183
11	1	1	172	179
	3		184	177
	5		367	366
	7		433	425
	9		538	519
	11		450	441
	13		305	486
	15		63	56
	17		245	241
	19		86	83
	21		95	94
11	1	2	179	172
	3		515	518
	5		578	567
	7		244	229
	9		87	88

Table 1. *(Continued)*

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
11	11	2	125	102	11	9	8	40	38	12	4	5	225	239	13	5	4	214	223	14	0	4	114	125
	13		400	380		11		61	59		6		49*	21		7		290	291		2		269	271
	15		234	218	11	1	9	186	196		8		133	143		9		111	106		4		185	192
	17		147	148		3		93	98		10		222	220		11		246	247		6		125	127
	19		96	90		5		110	118		12		34*	31		13		113	112		8		172	172
11	1	3	218	205		7		148	148		14		219	224		15		118	114		10		148	152
	3		341	333		9		222	227		16		36	17	13	1	5	220	225		12		221	229
	5		100	82	12	0	0	1354	1337	12	0	6	729	766		3		200	207	14	2	5	57	59
	7		189	181		2		112	106		2		97	107		5		166	181		4		98	99
	9		272	261		4		110	105		4		134	136		7		219	224		6		303	318
	11		363	334		6		348	347		6		269	280		9		79	86		8		138	148
	13		61*	50		8		221	215		8		280	285		11		97	90		10		118	132
	15		278	253		10		226	215		10		275	278		13		116	120	14	0	6	145	147
	17		237	237		12		583	568		12		271	284	13	1	6	173	180		2		100	97
	19		80	78		14		97	110		14		54	49		3		274	289		4		123	124
11	1	4	375	379		16		221	219	12	2	7	102	101		5		167	177		6		48	35
	3		352	362		18		511	516		4		267	271		7		163	170		8		277	291
	5		233	229	12	2	1	124	132		6		96	92		9		60	58	14	2	7	156	157
	7		315	301		4		344	337		8		79	81		11		212	225	15	1	1	233	233
	9		115	99		6		137	138		10		100	101	13	1	7	211	221		3		64	60
	11		359	339		8		535	520		12		211	220		3		268	280		5		245	244
	13		210	205		10		379	367	12	0	8	66	56		5		225	233		7		466	471
	15		100	88		12		216	213		2		161	166		7		149	155		9		382	388
	17		309	317		14		62	68		4		157	159		9		103	107		11		296	300
	19		138	140		16		62	41		6		256	261	13	1	8	77	73	15	1	2	78	76
11	1	5	533	555		18		166	171		8		178	181		3		53	53		3		280	288
	3		204	200	12	0	2	315	316	12	2	9	94	93	14	0	0	120	88		5		371	376
	5		266	266		2		147	140	13	1	1	104	98		2		264	251		7		195	198
	7		303	312		4		843	855		3		95	79		4		159	159		9		34*	26
	9		479	482		6		102	89		5		281	272		6		429	419		11		115	116
	11		146	148		8		154	163		7		328	329		8		399	391	15	1	3	155	150
	13		234	236		10		42*	40		9		336	323		10		122	117		3		282	287
	15		88	97		12		153	153		11		174	175		12		50	44		5		144	149
	17		294	303		14		364	358		13		244	235		14		154	370		7		116	124
11	1	6	193	195		16		285	291		15		131	134	14	2	1	140	139		9		281	292
	3		340	354		18		164	167		17		80	79		4		150	151	15	1	4	402	422
	5		307	324	12	2	3	168	165	13	1	2	123	116		6		178	176		3		346	359
	7		145	145		4		828	838		3		173	166		8		148	149		5		144	145
	9		100	95		6		61*	55		5		215	211		10		17*	22		7		227	236
	11		45*	42		8		334	315		7		72	89		12		33*	24	15	1	5	330	346
	13		52	51		10		171	161		9		108	113		14		143	139		3		195	199
	15		161	163		12		164	158		11		196	197	14	0	2	227	239		5		148	152
	17		210	212		14		475	465		13		106	113		2		376	368	16	0	0	1141	1169
11	1	7	343	347		16		304	310		15		125	133		4		112	126		2		91	98
	3		260	270		18		31*	26		17		68	74		6		71	68		4		282	285
	5		210	216	12	0	4	103	82	13	1	3	70	79		8		132	128		6		29*	11
	7		290	301		2		135	134		3		325	320		10		346	345	16	2	1	100	97
	9		93	91		4		135	140		5		199	199		12		108	113		4		202	215
	11		157	155		6		276	271		7		226	220		14		34	36		6		103	103
	13		292	304		8		603	603		9		234	226	14	2	3	164	164	16	0	2	146	141
	15		247	251		10		243	242		11		174	176		4		186	179		2		102	100
11	1	8	114	115		12		310	298		13		112	113		6		105	97		4		362	373
	3		186	186		14		56	59		15		213	219		8		91	91					
	5		301	304		16		79	71	13	1	4	240	240		10		171	171					
	7		188	192	12	2	5	52*	28		3		115	118		12		358	375					

* unobserved reflection

Several cycles of least-squares refinement in which individual form factors were used for Hg and Tl atoms and in which isotropic temperature factors for each atom were varied, reduced R to 11%. During these calculations, an equal weight was used for all reflections. Non-ionized atomic form factors given by IBERS, THOMAS *et al.*, THOMAS and UMEDA, FREEMAN and WATSON, and DAWSON were employed for Hg, Tl, Sb, As and S respectively (*International tables*, 1962). Additional cycles of least-squares refinement in which anisotropic temperature factors were varied, reduced R to 4.8% for all 1772 reflections. In the course of these calculations, individual weights calculated by the modified formula of GABE (1966) was used for each of the reflections:

$$w = \frac{1}{\sigma^2(F)} = 4F_o^2 \Big/ \sum_{i=1}^{4} \left\{\left(\frac{\partial F_o^2}{\partial q_i}\right)^2 \sigma^2(q_i)\right\},$$

where q_1 = peak count, q_2 = background count, $q_3 = (LP)^{-1}$ and q_4 = transmission. At the final stage, the effect of anomalous dis-

persion was taken into account for each atom, but no significant difference was found between enantiomorphic pair.

A block-diagonal least-squares program written by D. VAN DER HELM for the IBM 1620 computer, was used in the earlier stages. The same program, which was adapted and modified for the Bull Gamma 30 S by ENGEL (1968), was also used in the later stages. Table 1 gives the *hkl*, $|F_o|$ and $|F_c|$ values.

Description of the structure

The atomic coordinates and the temperature factors obtained are given in Tables 2*a* and 2*b*. The root-mean-square displacement of the atoms along the principal axes of the vibration ellipsoids are given in Table 3.

The difference in the atomic scattering factors being very small, it is not possible to distinguish mercury from thallium by x-ray diffraction measurements. However, the three heavy atoms in the general positions show two kinds of environments: the first heavy atom has two nearest sulfur atoms at about 2.4 Å, and the angle between these two bonds is about 166°, while the second and the third heavy atom have quite irregular coordinations and the distances between heavy

Table 2a

The final atomic coordinates of vrbaite, and their estimated standard deviations

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Hg (1)	0	0	0	—	—	—
Hg (2)	0.50323	0.05623	0.07614	0.00008	0.00003	0.00007
Tl (1)	0.25336	0.38707	0.20730	0.00010	0.00004	0.00009
Tl (2)	0.24997	0.27189	0.43836	0.00009	0.00004	0.00008
As (1)	0.24328	0.05352	0.09991	0.00015	0.00007	0.00015
As (2)	0.26024	0.04862	0.39537	0.00015	0.00007	0.00014
As (3)	0.50620	0.30217	0.40562	0.00017	0.00006	0.00013
As (4)	0.50094	0.29338	0.10902	0.00018	0.00006	0.00013
Sb	0.49086	0.15836	0.28910	0.00010	0.00004	0.00009
S (1)	0.1097	0.0906	0.0102	0.0003	0.0002	0.0004
S (2)	0.3828	0.4954	0.1801	0.0003	0.0002	0.0004
S (3)	0.5030	0.3643	0.2481	0.0007	0.0001	0.0004
S (4)	0.1266	0.4996	0.1761	0.0003	0.0002	0.0004
S (5)	0.3916	0.1662	0.4783	0.0003	0.0002	0.0004
S (6)	0.3839	0.2343	0.1880	0.0003	0.0002	0.0004
S (7)	0.2577	0.1185	0.2526	0.0005	0.0001	0.0004
S (8)	0.3594	0.4092	0.4777	0.0003	0.0002	0.0004
S (9)	0.1160	0.1571	0.4772	0.0003	0.0002	0.0004
S (10)	0.1144	0.2349	0.1715	0.0003	0.0002	0.0004

Table 2b. *The final anisotropic temperature-factor coefficients*

The values are the coefficients in the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}]$ (all values are multiplied by 10^5)

	β_{11}	$\sigma(\beta_{11})$	β_{22}	$\sigma(\beta_{22})$	β_{33}	$\sigma(\beta_{33})$	β_{12}	$\sigma(\beta_{12})$	β_{13}	$\sigma(\beta_{13})$	β_{23}	$\sigma(\beta_{23})$
Hg(1)	95	7	77	2	483	11	0	—	0	—	— 85	5
Hg(2)	140	7	116	2	576	10	126	5	—228	10	—182	4
Tl (1)	334	7	88	2	731	11	18	5	—44	15	102	5
Tl (2)	222	7	137	2	562	10	82	5	107	11	201	5
As (1)	101	10	31	3	223	14	—14	9	—25	18	7	8
As (2)	53	10	47	3	195	14	0	9	—16	18	9	8
As (3)	67	9	33	3	191	13	—26	9	—45	19	—5	7
As (4)	78	9	45	3	150	13	29	10	34	21	—6	7
Sb	189	8	45	2	294	11	—32	6	41	13	—86	5
S (1)	99	19	46	6	419	33	—12	20	—206	44	65	22
S (2)	77	19	79	7	314	30	52	18	—19	36	10	23
S (3)	238	19	35	5	258	24	—5	40	—70	44	26	19
S (4)	111	19	39	6	434	34	—16	18	50	39	—34	23
S (5)	98	19	59	7	245	28	—23	19	—35	37	—20	20
S (6)	96	19	64	7	205	28	—22	17	—11	36	8	20
S (7)	152	17	37	5	295	24	—38	30	—56	39	12	20
S (8)	89	19	80	7	309	30	—8	20	—7	38	—105	23
S (9)	139	21	61	7	369	32	—17	19	204	41	—92	23
S (10)	79	19	51	6	281	29	—6	17	—30	38	35	20

atoms and sulfur atoms are in the range of 3.1—3.7 Å. Since the former is one of the typical coordinations of mercury (GRDENIĆ, 1965), the former is concluded to be the mercury atom and the latter to be thallium atoms.

The structure thus determined confirms the chemical formula $Hg_3Tl_4As_8Sb_2S_{20}$ proposed by CAYE *et al.* Figures 4*a* and 4*b* show the structure of vrbaite parallel to *c* and *a* respectively. Vrbaite contains two kinds of mercury atoms. The first of them, Hg(1) is surrounded tetrahedrally by four sulfur atoms at distances of 2.570 and 2.581 Å. Examples of this coordination are found in the structures of metacinnabarite, HgS (Hg—S = 2.55 Å, BUCKLEY and VERNON, 1925), mercury tetrathiocyanate-copper diethylene-diamine $[Hg(SCN)_4]$-$[Cu(en)_2]$ (Hg—S = 2.56 Å, SCOULOUDI, 1953) and some other materials. Hg(2) has two nearest S atoms at distances of 2.38 Å and forms a bent bond (S—Hg—S = 166.0°). This kind of coordination is the most common configuration of mercury and is found in cinnabarite, HgS (Hg—S = 2.36 Å, S—Hg—S = 172°; AURIVILLIUS, 1950), livingstonite, $HgSb_4S_8$ (Hg—S = 2.35 Å, S—Hg—S = 180°; NIIZEKI and

BUERGER, 1957) and many other compounds. The angles between two Hg—S bonds are variable in the different compounds.

Table 3. *The root-mean-square displacements of the atoms along the principal axes of the vibration ellipsoids and direction cosines of these axes with respect to the crystallographic axes*

	$B_{\text{isotrop.}}$	Axes	B	$\sqrt{\overline{u^2}}$	cos α_1	cos α_2	cos α_3
Hg(1)	1.62 Å^2	1	0.68 Å^2	0.093 Å	1.000	0	0
		2	1.49	0.137	0	0.906	0.421
		3	2.67	0.183	0	−0.421	0.906
Hg(2)	2.16	1	0.63	0.089	0.938	−0.311	0.150
		2	1.78	0.150	0.129	0.720	0.681
		3	4.07	0.227	−0.320	−0.619	0.716
Tl (1)	2.68	1	2.42	0.175	0.972	0.232	0.003
		2	1.75	0.149	−0.222	0.936	−0.271
		3	3.88	0.221	−0.066	0.263	0.962
Tl (2)	2.48	1	1.42	0.134	0.940	−0.336	0.040
		2	4.13	0.228	0.228	0.717	0.658
		3	1.90	0.155	−0.250	−0.609	0.751
As (1)	0.85	1	0.60	0.087	0.600	0.799	0.023
		2	0.78	0.099	−0.774	0.588	−0.233
		3	1.16	0.121	−0.200	0.121	0.972
As (2)	0.80	1	0.37	0.068	0.997	−0.009	0.071
		2	1.07	0.116	−0.031	0.840	0.541
		3	0.96	0.110	−0.065	−0.542	0.837
As (3)	0.72	1	0.35	0.067	0.874	0.434	0.217
		2	0.80	0.100	−0.403	0.898	−0.172
		3	1.01	0.113	−0.270	0.062	0.960
As (4)	0.77	1	0.46	0.076	0.887	−0.327	−0.325
		2	1.06	0.116	0.351	0.935	0.017
		3	0.79	0.100	0.299	−0.130	0.945
Sb	1.28	1	1.28	0.127	0.904	0.047	−0.423
		2	0.70	0.094	0.172	0.866	0.467
		3	1.85	0.153	0.389	−0.496	0.776
S(1)	1.29	1	0.47	0.077	0.924	−0.096	0.367
		2	0.94	0.109	0.176	0.966	−0.188
		3	2.44	0.176	−0.336	0.239	0.910

Table 3. *(Continued)*

	$B_{isotrop.}$	Axes	B	$\sqrt{\overline{u^2}}$	cos α_1	cos α_2	cos α_3
S(2)	1.29	1	0.46	0.076	0.965	− 0.251	0.065
		2	1.82	0.151	0.236	0.954	0.181
		3	1.59	0.142	− 0.107	− 0.159	0.981
S(3)	1.26	1	1.80	0.151	0.907	− 0.076	− 0.413
		2	0.74	0.097	− 0.028	0.970	− 0.241
		3	1.25	0.125	0.420	0.230	0.877
S(4)	1.29	1	0.73	0.096	0.822	0.568	− 0.015
		2	0.90	0.107	− 0.556	0.811	0.178
		3	2.25	0.168	0.114	− 0.138	0.983
S(5)	1.08	1	0.65	0.091	0.948	0.236	0.210
		2	1.21	0.123	− 0.304	0.507	0.805
		3	1.39	0.132	0.083	− 0.828	0.553
S(6)	1.05	1	0.66	0.091	0.980	0.164	0.103
		2	1.45	0.135	− 0.178	0.973	0.145
		3	1.04	0.114	− 0.076	− 0.161	0.983
S(7)	1.13	1	0.67	0.092	0.535	0.842	0.056
		2	1.12	0.119	− 0.738	0.499	− 0.452
		3	1.60	0.142	− 0.409	0.200	0.890
S(8)	1.31	1	0.63	0.089	0.993	0.092	0.069
		2	1.09	0.118	− 0.112	0.637	0.762
		3	2.22	0.167	0.026	− 0.764	0.643
S(9)	1.40	1	0.64	0.090	0.830	− 0.233	− 0.505
		2	1.15	0.120	0.399	0.882	0.248
		3	2.42	0.175	0.388	− 0.408	0.826
S(10)	1.04	1	0.56	0.084	0.994	0.011	0.104
		2	1.03	0.114	0.032	0.913	− 0.405
		3	1.54	0.139	− 0.099	0.406	0.908

The two thallium atoms show irregular coordinations; that is, the interatomic distances between thallium and sulfur atoms have a wide range (Table 4). When distances shorter than 3.75 Å (Tl—Tl distance, *International tables*) are taken into account, the Tl(1) atom is surrounded by two S atoms at distances of 3.086 and 3.152 Å, and by five S atoms at distances between 3.346 and 3.433 Å. Tl(2) is surrounded by three

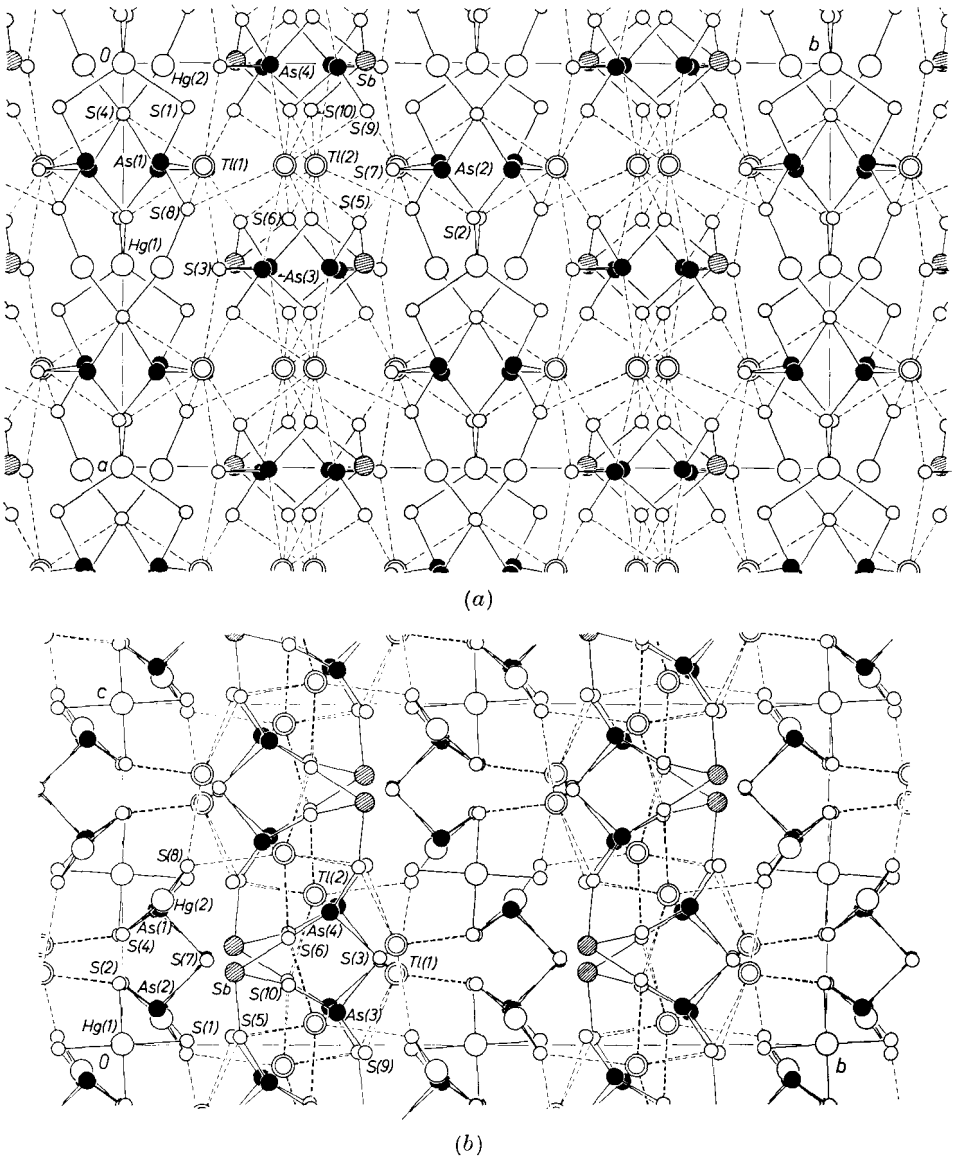

Fig. 4. The structure of vrbaite. (*a*) Projection along the *c* axis. (*b*) Projection along the *a* axis

S atoms at distances between 3.148 and 3.259 Å, and by four S and two As atoms at distances between 3.322 and 3.622 Å. The mean values of the Tl—S distances are 3.32 Å for Tl(1) and 3.37 Å for Tl(2).

The environment of both the thallium atoms are, however, somewhat similar, when the longer distances (≤ 4 Å) are included, Fig. 5. Eight sulfur atoms around Tl(1) [or Tl(2)] make a distorted cube which is similar to the CsCl structure, and two S (or two As) atoms are situated in the direction perpendicular to one of the three sets of opposite faces. A few structures of sulfides and sulfosalts which contain thallium have so far been investigated (Table 6), and the coordination around thallium shows diversity in these kinds of compounds.

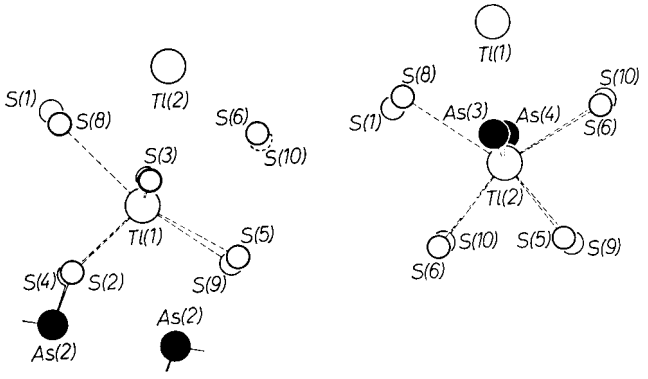

Fig. 5. The environment of thallium atoms. The broken circle indicates the sulfur atom which has slightly longer distance than 4 Å

In TlS, there are two kinds of thallium atoms (Scatturin and Frasson, 1956). Tl(1) is at the center of a tetrahedron of four sulfur atoms and the Tl(1)—S distances, being covalent bonds, are 2.59 Å. Tl(2) is surrounded by eight S atoms [Tl(2)—S = 3.33 Å] which form a square antiprism. The sulfur atoms around $(Tl, Pb)_{II}$ in hutchinsonite, $(Tl,Pb)_2As_5S_9$, (Takéuchi, Ghose and Nowacki, 1965) has a similar configuration to that around Tl(1) in vrbaite, but the former lacks one sulfur atom at a corner of the cube. Hatchite $PbTlAgAs_2S_5$ (Marumo and Nowacki, 1967) and wallisite $PbTlCuAs_2S_5$ (Takéuchi, Ohmasa and Nowacki, 1968), are isotypic and the distances between Tl and S atoms are irregular. Seven sulfur atoms make a distorted pentagonal bipyramid, but one arsenic atom is also located close to the thallium atom (3.4 Å). The mean values of the Tl—S distances of the above materials are in the range of 3.3—3.4 Å. This is close to the sum of the ionic radii of Tl^+ and S^{2-} (= 3.32 Å; Wyckoff, 1948) and suggests that the bonding of thallium should be ionic in these structures. If a thallium atom is surrounded by isolated anions, the arrangement of anions is

Table 4. *Interatomic distances in vrbaite* [in Å]

	S(1)	S(2)	S(3)	S(4)	S(5)	S(6)	S(7)	S(8)	S(9)	S(10)	Mean	Hg(2)	Tl(2)	As(3)	As(4)
Hg(1)	2.581 (0.004)	2.570 (0.004)									2.58				
Hg(2)				2.399 (0.004)				2.366 (0.004)	2.864 (0.004)		2.38	3.142 (0.001)			
Tl(1)		3.086 (0.004)	3.417 (0.008)	3.152 (0.004)	3.416 (0.004)			3.406 (0.004)	3.346 (0.004)		3.32		3.749 (0.001)		
			3.433 (0.008)												
Tl(2)					3.148 (0.004)	3.461 (0.004)		3.558 (0.005)	3.259 (0.004)	3.622 (0.004)	3.37			3.525 (0.002)	3.415 (0.002)
						3.343 (0.004)				3.200 (0.004)	3.39*				
As(1)	2.232 (0.004)						2.305 (0.004)	2.254 (0.004)			2.26				
As(2)		2.228 (0.004)		2.273 (0.004)			2.295 (0.004)				2.27				
As(3)			2.297 (0.004)						2.195 (0.005)	2.310 (0.004)	2.27				
As(4)			2.284 (0.004)		2.283 (0.004)	2.272 (0.004)					2.28				
Sb					2.522 (0.004)	2.551 (0.004)				2.478 (0.004)	2.52				

* The distances for the As(3) and the As(4) are taken into account for the calculation of the mean value.

Table 5. *Bond angles in vrbaite*

S(1)—Hg(1)—S(1′)	110.6°	(0.2°)
S(1)—Hg(1)—S(2)	110.3	(0.1)
S(1)—Hg(1)—S(2′)	110.4	(0.1)
S(2)—Hg(1)—S(2′)	104.7	(0.2)
Mean	109.3	
S(4)—Hg(2)—S(8)	165.9	(0.8)
S(1)—As(1)—S(7)	98.6	(0.2)
S(1)—As(1)—S(8)	97.2	(0.2)
S(7)—As(1)—S(8)	98.3	(0.2)
Mean	98.0	
S(2)—As(2)—S(4)	99.4	(0.2)
S(2)—As(2)—S(7)	98.0	(0.2)
S(4)—As(2)—S(7)	95.6	(0.2)
Mean	97.7	
S(3)—As(3)—S(9)	101.8°	(0.2°)
S(3)—As(3)—S(10)	98.7	(0.2)
S(9)—As(3)—S(10)	95.9	(0.2)
Mean	98.8	
S(3)—As(4)—S(5)	98.7	(0.2)
S(3)—As(4)—S(6)	100.4	(0.2)
S(5)—As(4)—S(6)	93.5	(0.2)
Mean	97.5	
S(5)—Sb—S(6)	91.8	(0.1)
S(5)—Sb—S(10)	98.5	(0.1)
S(6)—Sb—S(10)	87.3	(0.2)
Mean	92.5	

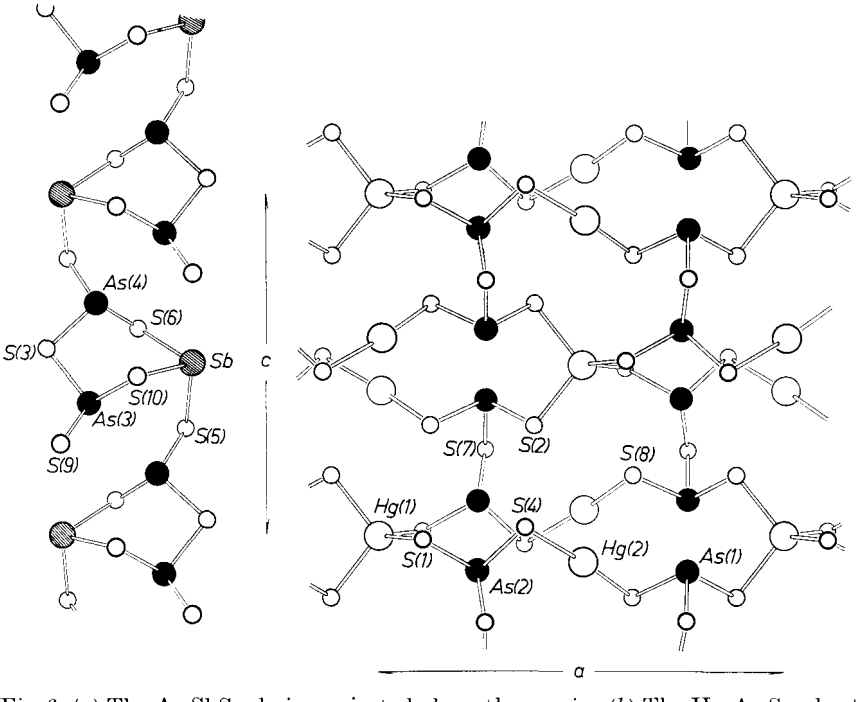

Fig. 6. (*a*) The As_2SbS_5 chain projected along the *a* axis. (*b*) The $Hg_3As_4S_{10}$ sheet projected along the *b* axis

Table 6. Tl—S *distances in various compounds**

vrbaite		hatchite	
Tl(1)—S	3.086 Å	Tl—S	3.05 Å
	3.152		3.12
	3.346		3.46
	3.406		3.46
	3.416		3.53
	3.417		3.61
	3.433		3.65
		—As	(3.48)
Mean	3.32	Mean	3.41
			(3.42)
Tl(2)—S	3.148 Å	wallisite	
	3.200	Tl—S	2.99 Å
	3.259		3.14
	3.343		3.35
	3.461		3.46
	3.558		3.51
	3.622		3.57
—As	(3.415)		3.64
	(3.525)	—As	(3.37)
Mean	3.37	Mean	3.38
	(3.39)		(3.38)
hutchinsonite		TlS	
Tl—S	3.12 Å	Tl(1)—S	2.59Å**
	3.15	Tl(2)—S	3.33
	3.30		
	3.31		
	3.33		
	3.37		
	3.43		
Mean	3.29		

* Tl—S distances in lorandite ($TlAsS_2$, ZEMANN and ZEMANN, 1959) were excluded from this table, because the refinement is not sufficient and As—S distances in lorandite deviate from normal values.

** This bonding may be covalent.

mainly affected by the ratio of the radius of an anion to that of a cation and bond distances between the cation and the anions are uniform. The thallium atoms in sulfosalts have an environment of rigid groups in which all atoms are bound by covalent bonds. Therefore, the distances between thallium atoms and anions are not kept uni-

form, and the arrangement of sulfur atoms around thallium atoms are variable in each compound.

The polyhedra formed by the sulfur atoms around the antimony and arsenic atoms are flat trigonal pyramids, which are quite common in the structures of sulfosalts (NOWACKI, 1969, 1970). The mean distances of Sb—S and As—S bonds are 2.52 Å and 2.27 Å respectively. The temperature factors of both atoms, having normal values, suggest that Sb and As atoms are in an ordered state.

The structure of vrbaite is characterized by infinite As_2SbS_5 chains parallel to the c axis, and by $Hg_3As_4S_{10}$ sheets perpendicular to the b axis. The former consists of one Sb pyramid and of two pyramids of As atoms, Fig. 6*a*. This is the first example of chains composed of both Sb and As pyramids. The latter is composed of one mercury tetrahedron, two nonlinear groups of mercury and four arsenic pyramids, Fig. 6*b*. The As_2SbS_5 chains sandwich Tl atoms and make slabs perpendicular to the b axis. These slabs and $Hg_3As_4S_{10}$ sheets, sandwiching the other Tl atoms, are arranged alternately along the b direction. This characteristic feature of the structure explains well the good cleavage parallel to (010).

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References

K. L. AURIVILLIUS (1950), On the crystal structure of cinnabar. Acta Chem. Scand. **4**, 1413—1436.

W. L. BOND (1951), Making small spheres. Rev. Scient. Instr. **22**, 344—345.

H. E. BUCKLEY and W. S. VERNON (1925), The crystal-structures of the sulphides of mercury. Min. Mag. **20**, 382—392.

R. CAYE, P. PICOT, R. PIERROT et F. PERMINGEAT (1967), Nouvelles données sur la vrbaite, sa teneur en mercure. Bull. Soc. franç. Minéral. Cristallogr. **90**, 185—191.

P. ENGEL (1968), Kristallographische Programme für die Rechenanlage Bull Gamma 30. [Unpublished Appendix to Diss. Univ. Bern.]

C. FRONDEL (1941), Unit cell and space group of vrbaite [Tl(As,Sb)$_3$S$_4$], seligmannite (CuPbAsS$_3$) and samsonite (Ag$_4$MnSb$_2$S$_6$). Amer. Min. **26**, 25—28.

E. J. GABE (1966), 1620 programs from I.C.R. Department of Molecular Structure (Physics Department), I.C.R. No. 16, data reduction. Appendix.

D. GRDENIĆ (1965), The structural chemistry of mercury. Quart. Rev. **19**, 303—328.

International tables for x-ray crystallography, Vol. III (1962), 201—212, Kynoch Press, Birmingham.

B. JEŽEK (1912), Vrbaite, ein neues Thalliummineral von Allchar in Macedonien. Z. Kristallogr. **51**, 365—378.

FR. KŘEHLÍK (1912), Chemische Untersuchung des Vrbaits. Z. Kristallogr. **51**, 379—383.

F. MARUMO and W. NOWACKI (1967), The crystal structure of hatchite, PbTlAgAs$_2$S$_5$. Z. Kristallogr. **125**, 249—265.

N. NIIZEKI and M. J. BUERGER (1957), The crystal structure of livingstonite, HgSb$_4$S$_8$. Z. Kristallogr. **109**, 129—157.

W. NOWACKI (1968), Über Hatchit, Lengenbachit und Vrbait. N. Jahrb. Mineral., Monatsh., 69—75.

W. NOWACKI (1969), Zur Klassifikation und Kristallchemie der Sulfosalze. Schweiz. Min. Petr. Mitt. **49**, 109—156.

W. NOWACKI (1970), Zur Klassifikation der Sulfosalze. Acta Crystallogr. B **26**, 286—289.

CHARLES PALACHE, HARRY BERMAN and CLIFFORD FRONDEL (1944), *The system of mineralogy*, Vol. 1, 484—485. Seventh edition, John Wiley and Sons, New York.

V. SCATTURIN e E. FRASSON (1956), Solfuri di tallio da polisolfuro ammonico: formazione e struttura del monosolfuro di tallio TlS. Ric. Sci. **26**, 3382 [SR. **20**, 192].

H. SCOULOUDI (1953), The crystal structure of mercury tetrathiocyanate-copper diethylenediamine, [Hg(SCN)$_4$][Cu(en)$_2$]. Acta Crystallogr. **6**, 651—657.

Y. TAKÉUCHI, S. GHOSE and W. NOWACKI (1965), The crystal structure of hutchinsonite, (Tl,Pb)$_2$As$_5$S$_9$. Z. Kristallogr. **121**, 321—348.

Y. TAKÉUCHI, M. OHMASA and W. NOWACKI (1968), The crystal structure of wallisite, PbTlCuAs$_2$S$_5$, the Cu analogue of hatchite, PbTlAgAs$_2$S$_5$. Z. Kristallogr. **127**, 349—365.

R. W. G. WYCKOFF (1948), *Crystal structures*. Interscience, New York.

A. ZEMANN und J. ZEMANN (1959), Zur Kenntnis der Kristallstruktur von Lorandit, TlAsS$_2$. Acta Crystallogr. **12**, 1002—1006.