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The Crystal Structures of KHg and KHg_2

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The crystal structures of KHg and KHg_2 have been determined. KHg has a triclinic unit cell with $a = 6{\cdot}59$ Å, $b = 6{\cdot}76$ Å, $c = 7{\cdot}06$ Å, $\alpha = 106° 5'$, $\beta = 101° 52'$ and $\gamma = 92° 47'$. KHg_2 has an orthorhombic unit cell with $a = 8{\cdot}10$ Å, $b = 5{\cdot}16$ Å and $c = 8{\cdot}77$ Å. The mercury atoms are in slightly distorted square planar groups of four in both structures. In KHg the groups are connected to form chains, and in KHg_2 they are bonded together to form a three-dimensional network. KHg_2 can be described as having a distorted aluminum boride structure.

Introduction

The compounds in the K–Hg system have been studied as part of a program to investigate the compounds formed between the alkaline, alkaline earth metals, and the elements in group II-B. The structures of KHg and KHg_2 have been solved, and X-ray diffraction data have been obtained of KHg_{11}, and of a phase tentatively labeled K_5Hg_7. Powder diagrams of $BaHg_{11}$, $SrHg_{11}$ and $RbHg_{11}$ have shown that these compounds are isostructural with KHg_{11}. The structure of $BaHg_{11}$ has been reported (Peyronel, 1952). There is much confusion in the literature as to the number and compositions of the potassium amalgams, and further work is necessary to establish the number and structure of the remaining potassium–mercury compounds.

Experimental procedure

The K–Hg compounds are very reactive with respect to the oxygen and water in the air; therefore, the compounds and samples for X-ray work were prepared in an inert atmosphere. Generally, the samples were prepared in a reaction vessel which was continually flushed with dry nitrogen. The reaction is very exothermic, so little or no heating was required.

Powder samples were prepared in a dry box which was flushed with dry nitrogen. A microscope could be fitted into the dry box for separating single crystals, but usually single crystals were obtained by directly removing them from the reaction vessel. This was accomplished by drawing them into a long capillary, coated on the inside with wax, which was connected to a vacuum pump. The capillary was sealed in a flame on both ends and examined for crystals or fragments of crystals. If a suitable crystal was found, it was stuck to the wax by gentle heating. The capillary was then sealed off on either side of the crystal.

Multiple films were placed in the Weissenberg camera and a series of three or four timed exposures was usually taken for each set of data on the precession camera. The intensities were visually estimated by comparison with a graduated scale.

The precession camera was calibrated with sodium chloride powder diagrams in order to obtain a more precise value for the film-to-crystal distance. For the particular camera used, $d = 5{\cdot}984 \pm 0{\cdot}008$ cm.

KHg

KHg is a gold-colored compound with a melting point of 178° C. From precession camera data, the unit cell was found to be triclinic with

$$a = 6{\cdot}59,\ b = 6{\cdot}76,\ c = 7{\cdot}06\ \text{Å},$$
$$\alpha = 106° 5',\ \beta = 101° 52',\ \gamma = 92° 47',$$
$$V = 294\ \text{Å}^3,\ D_X = 5{\cdot}41,\ Z = 4,\ D_m\ (\text{Mäey, 1899}) = 5{\cdot}47\ .$$

The space group $P\bar{1}$ was assumed.

Rough values of the x and y parameters of mercury were obtained by trial and error from the ($hk0$) data. A Patterson projection using ($0kl$) data was constructed, from which approximate values of the z parameters of mercury were determined. The parameters were refined by means of electron-density projections on (100) and (001) (Fig. 1).

The potassium positions were determined by a combination of spatial requirements, electron-density maps and least-squares refinement. The low scattering power of potassium relative to mercury atoms made it difficult to determine potassium positions directly from the electron-density projections. Both the (001) and (100) plots contained more minor peaks than would be expected for potassium atoms. Attempts were made to choose positions for potassium atoms based on pairs of these peaks which would give reasonable interatomic distances. In the (100) projection, peaks near the b axis ($z = 0$) could be easily eliminated on spatial grounds, as well as a peak near the mercury atom at $z = 0{\cdot}29$. Plausible distances could be found

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with the potassium atoms K_1 at x_1, 0·653, 0·489 and K_2 at x_2, 0·794, 0·166, corresponding to two peaks in the (100) projection. Spatial requirements suggested

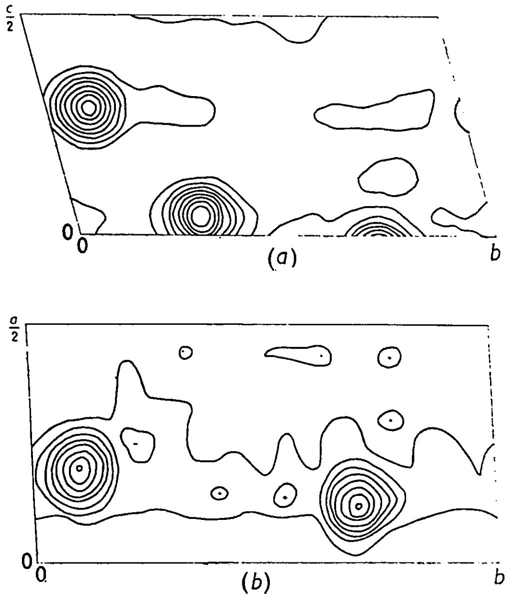

Fig. 1. Projection of the electron density of KHg (*a*) on to (100), (*b*) on to (001).

that the x parameters should be $x_1 = 0{\cdot}285$ and $x_2 = 0{\cdot}670$. No combinations of the minor peaks in the (001) projection led to reasonable positions, although an indication of the position of the K_2 atom is present.

In order to obtain, perhaps, an improved estimate of the x parameters of the potassium atoms, corrections to the assumed x parameters were calculated by the least-squares method, holding all other coordinates and atoms at the parameter values already determined

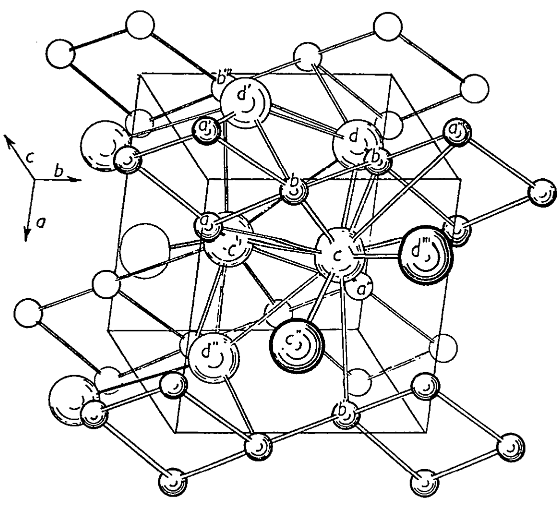

Fig. 2. The structure of KHg. The small circles represent Hg atoms.

from the electron-density maps. The shifts, −0·004 and 0·005 parameter units, were less than the limit of error estimated for the potassium positions.

The errors in the parameters due to random errors in the F_o's were estimated by Cruickshank's method (1949). For the potassium parameters, the errors estimated in this way agreed very well with the error estimated from the least-squares method. The standard errors are ±0·005 Å for the Hg positions and ±0·05 Å for the K positions.

In space group $P\bar{1}$, the atomic positions are: x, y, z; $\bar{x}, \bar{y}, \bar{z}$ with

	x	y	z
Hg_1	0·198	0·101	0·286
Hg_2	0·877	0·303	0·049
K_1	0·281	0·653	0·489
K_2	0·675	0·794	0·166

The interatomic distances are listed in Table 1. The structure is shown in Fig. 2.

Table 1. *Interatomic distances for* KHg

Atom	Ligand	Distance (Å)	Key (see Fig. 2)
Hg_1	Hg	3·02	*a′b*
	Hg	3·04	*ab*
	K	3·58	*ac*
	K	3·58	*a″c*
	K	3·70	*a‴c*
	K	3·75	*a′d′*
Hg_2	Hg	3·02	*ba′*
	Hg	3·04	*ba*
	Hg	3·36	*bb′*
	K	3·56	*b″c*
	K	3·58	*b‴d*
	K	3·59	*bd*
	K	3·60	*bd′*
	K	3·67	*bc*
K_1	Hg	3·56	*cb″*
	Hg	3·58	*ca″*
	Hg	3·59	*ca*
	Hg	3·68	*cb*
	Hg	3·72	*ca‴*
	K	3·65	*cc′*
	K	4·03	*cd*
	K	4·21	*cc″*
	K	4·36	*cd″*
	K	4·46	*cd‴*
K_2	Hg	3·58	*db‴*
	Hg	3·59	*db*
	Hg	3·60	*d′b*
	Hg	3·70	*db′*
	Hg	3·75	*d′a′*
	K	4·03	*dc*
	K	4·36	*d″c*
	K	4·46	*d‴c*

The discrepancy factor, $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$, is 0·28 for the ($hk0$) data (0·15 for observed reflections only). The temperature factor, B, is 3·57 Å^2 for the ($hk0$) data and 4·44 Å^2 for the ($0kl$) data. F_o and F_c are listed in Table 2.

Table 2. *Calculated and observed structure factors for* KHg

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
010	60	61	430	0	14	$02\bar{2}$	175	−203
020	99	−93	440	0	11	$02\bar{3}$	122	−121
030	57	57	450	0	13	$02\bar{4}$	0	11
040	58	−53	$\bar{5}10$	62	93	$02\bar{5}$	16	−21
050	134	−111	$\bar{5}20$	55	33	$02\bar{6}$	61	−63
060	0	− 8	$\bar{5}30$	52	−77	$02\bar{7}$	0	5
070	0	4	$\bar{5}40$	0	−12	030	59	54
$\bar{1}10$	0	− 9	$\bar{5}50$	0	−14	031	25	−21
$\bar{1}20$	140	161	$\bar{5}60$	39	−63	032	129	131
$\bar{1}30$	187	170	500	0	− 1	033	101	79
$\bar{1}40$	40	63	510	46	36	034	0	8
$\bar{1}50$	65	−56	520	59	68	035	22	12
$\bar{1}60$	0	5	530	0	−25	036	29	28
$\bar{1}70$	0	−30	540	43	−46	$03\bar{1}$	160	148
100	114	131	$\bar{6}10$	78	90	$03\bar{2}$	58	64
110	0	15	$\bar{6}20$	0	5	$03\bar{3}$	81	−75
120	211	−232	$\bar{6}30$	0	2	$03\bar{4}$	36	31
130	55	−55	$\bar{6}40$	44	53	$03\bar{5}$	0	− 9
140	0	22	$\bar{6}50$	0	−15	$03\bar{6}$	60	−55
150	80	−73	$\bar{6}60$	39	−45	$03\bar{7}$	33	−42
160	0	− 4	600	0	20	040	40	−47
170	60	53	610	41	−46	041	22	−25
$\bar{2}10$	165	−157	620	0	− 2	042	25	15
$\bar{2}20$	103	108	630	0	−19	043	22	−25
$\bar{2}30$	160	141	$\bar{7}10$	0	10	044	61	−62
$\bar{2}40$	0	25	$\bar{7}20$	0	−14	045	0	− 3
$\bar{2}50$	32	41	$\bar{7}30$	0	34	$04\bar{1}$	111	119
$\bar{2}60$	62	40	$\bar{7}40$	41	51	$04\bar{2}$	107	93
$\bar{2}70$	0	−31	700	0	6	$04\bar{3}$	0	− 1
200	142	−138	710	55	−58	$04\bar{4}$	44	35
210	0	13	001	76	92	$04\bar{5}$	75	85
220	118	−111	002	31	3	$04\bar{6}$	0	20
230	87	−85	003	107	81	$04\bar{7}$	0	3
240	84	74	004	79	77	050	101	−92
250	37	33	005	47	−49	051	23	−22
260	0	2	006	0	− 6	052	0	4
$\bar{3}10$	142	−142	007	0	11	053	43	−44
$\bar{3}20$	0	−14	010	60	61	054	21	−18
$\bar{3}30$	0	−35	011	116	−135	$05\bar{1}$	25	−39
$\bar{3}40$	0	−28	012	151	−142	$05\bar{2}$	0	12
$\bar{3}50$	66	92	013	17	10	$05\bar{3}$	63	−69
$\bar{3}60$	46	65	014	109	−82	$05\bar{4}$	48	−52
$\bar{3}70$	0	−15	015	108	−85	$05\bar{5}$	36	33
300	160	−122	016	25	−16	$05\bar{6}$	0	16
310	44	41	017	0	12	$05\bar{7}$	0	−10
320	0	26	$01\bar{1}$	53	50	060	0	− 7
330	0	−16	$01\bar{2}$	125	−127	061	32	42
340	91	72	$01\bar{3}$	54	62	062	31	43
350	63	64	$01\bar{4}$	148	141	$06\bar{1}$	17	−22
360	0	−16	$01\bar{5}$	21	40	$06\bar{2}$	24	29
$\bar{4}10$	0	−11	$01\bar{6}$	17	9	$06\bar{3}$	22	11
$\bar{4}20$	0	17	$01\bar{7}$	48	49	$06\bar{4}$	40	−42
$\bar{4}30$	103	−129	020	94	−92	$06\bar{5}$	0	−15
$\bar{4}40$	86	−84	021	171	−166	$06\bar{6}$	0	0
$\bar{4}50$	46	42	022	0	0	070	0	4
$\bar{4}60$	0	8	023	85	81	071	28	35
$\bar{4}70$	0	3	024	16	−14	$07\bar{1}$	0	0
400	62	−56	025	0	−10	$07\bar{2}$	36	44
410	73	74	026	46	43	$07\bar{3}$	30	50
420	111	97	$02\bar{1}$	45	−22	$07\bar{4}$	0	1

KHg_2

KHg_2 is a silvery, hard compound with a melting point of 278° C. The unit cell is orthorhombic with

$a = 8{\cdot}10,\ b = 5{\cdot}16,\ c = 8{\cdot}77$ Å,
$V = 398$ Å^3, $D_X = 7{\cdot}88$, $Z = 4$, and D_m (Mäey, 1899) $= 7{\cdot}95$.

The reflections observed were those characteristic of the space groups *Im2a* and *Imma*. The latter space group was assumed for preliminary work. The agreement subsequently obtained between F_o and F_c indicated that the correct space group had been chosen.

For the space group *Imma* there is only one eightfold set in which the eight mercury atoms may be placed. Other sets are incompatible with the spatial requirements of the mercury atoms in the (010) direction. Similarly, spatial requirements clearly indicated the set in which the potassium atoms should be placed. The positions are:

$$(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$$
$$8\ \mathrm{Hg\ in}\ (i){:}\ x, \tfrac{1}{4}, z;\ \bar{x}, \tfrac{3}{4}, \bar{z};\ \bar{x}, \tfrac{1}{4}, z;\ x, \tfrac{3}{4}, \bar{z};$$
$$4\ \mathrm{K\ in}\ (e){:}\ 0, \tfrac{1}{4}, z;\ 0, \tfrac{3}{4}, \bar{z}.$$

Approximate values for the mercury parameters were obtained by inspection of $(0kl)$ and $(h0l)$ data. The mercury parameters and potassium z parameters were refined by electron-density projections on (010) (Fig. 3). A spurious peak of comparable magnitude to

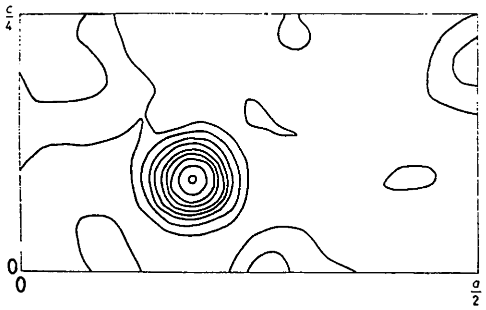

Fig. 3. Projection of the electron density of KHg_2 on to (010).

the potassium peak occurs in this electron-density projection at (0·27, 0). This position places an atom impossibly close to the mercury atoms. It is probable that this peak is a ripple from the mercury peak due to the finite-series approximation. The parameters are:

$$\mathrm{Hg}{:}\ x = 0{\cdot}190,\ z = 0{\cdot}087;$$
$$\mathrm{K}{:}\ \ z = 0{\cdot}703\,.$$

Table 3. *Interatomic distances in* KHg_2

Atom	Ligand	Distance (Å)	Key (see Fig. 4)
Hg	2 Hg	3·00	*af, ab, cd, de*
	Hg	3·02	*bc, b′c′*
	Hg	3·08	*aa′, bb′*
	2 K	3·52	*bg, b′g, fg, f′g*
	K	3·57	*d′g, dg*
	K	3·70	*ag, a′g*
	2 K	3·74	*eg, e′g, cg, c′g*
K	4 Hg	3·52	*gb′, gb, gf, gf′*
	2 Hg	3·57	*gd, gd′*
	2 Hg	3·70	*ga, ga′*
	4 Hg	3·74	*ge, ge′, gc, gc′*
	2 K	4·13	*gg′, gg″*

The interatomic distances and the structure are shown in Table 3 and Fig. 4. The list of F_o and F_c values is given in Table 4.

An estimate was made of the error in the atomic positions, due to random errors in the F_o's, by Cruickshank's method. The errors are ±0·003 Å for mercury and ±0·06 Å for potassium. Discrepancy factors for the $(0kl)$ and $(h0l)$ data are 0·15 and 0·29 (0·15 and 0·18 for observed reflections only). The value of the temperature constant, B, is 1·02 Å² and 1·69 Å² for the $(h0l)$ and $(0kl)$ data.

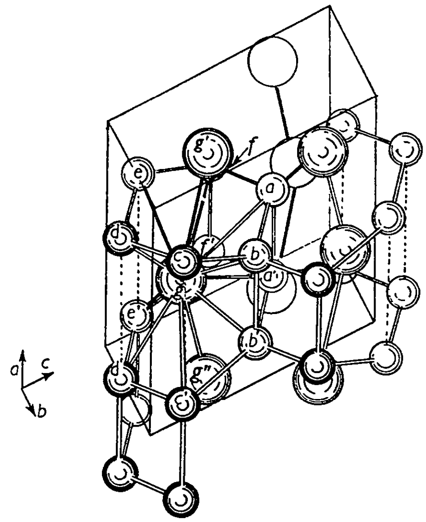

Fig. 4. The structure of KHg_2. The small circles represent Hg atoms.

Other K–Hg compounds

Single-crystal data have been obtained of a phase tentatively labelled K_5Hg_7. The unit cell is orthorhombic with

$$a = 9{\cdot}99,\ b = 19{\cdot}23,\ c = 8{\cdot}25\ \text{Å},$$
$$V = 1585\ \text{Å}^3,\ D_X = 6{\cdot}70,\ Z = 4,\ \text{and}\ D_m = 6{\cdot}61.$$

The absences are characteristic of the space group *Pbcm*. Interpretation of the data is in progress.

KHg_{11} has been shown by powder diagrams to be isostructural with $RbHg_{11}$, $SrHg_{11}$ and $BaHg_{11}$. The structure of $BaHg_{11}$ has been reported by Peyronel (1952). (Ketelaar (1937) reported that KHg_{11} was cubic with 36 atoms in the unit cell.) The cell dimensions of these compounds are given in Table 5.

Further work is necessary to establish the composition and number of other potassium–mercury compounds.

Discussion of results

On the basis of the structures of KHg and KHg_2, it appears that the mercury atoms tend to take positions in square planar groups. This has also been observed in some Na–Hg compounds (Nielsen & Baenziger, 1954). The Hg–Hg distances between atoms in a group are essentially the same as the shortest distances between atoms in solid mercury.

In KHg, the plane group of mercury atoms is not quite square but distorted to a parallelogram with an angle of 93° 34′. The interatomic distances are 3·04 and 3·02 Å, with opposite sides equal. The plane groups are connected to each other by a Hg–Hg bond

Table 4. *Calculated and observed structure factors for* KHg_2

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
002	246	210	062	71	−68	408	0	−22
004	294	−249	064	90	87	4,0,10	0	26
006	368	−348	066	121	133	501	239	319
008	96	−105	071	68	81	503	0	2
0,0,10	117	148	073	147	117	505	376	−312
0,0,12	93	124	002	248	212	507	221	−179
011	272	−360	004	304	−257	509	0	34
013	447	−457	006	339	−376	5,0,11	182	156
015	173	−159	008	89	−120	600	208	269
017	200	176	0,0,10	115	184	602	95	78
019	183	234	0,0,12	164	158	604	120	−108
020	465	−541	101	218	170	606	216	−170
022	247	−174	103	0	29	608	88	−64
024	269	215	105	178	−197	6,0,10	82	97
026	302	303	107	0	−70	701	91	−133
028	84	94	109	0	9	703	0	31
0,2,10	101	−134	1,0,11	—	71	705	91	90
031	212	243	200	302	−348	707	111	100
033	424	340	202	323	−222	709	0	−25
035	119	121	204	197	205	800	170	−252
037	157	−139	206	259	273	802	134	−144
039	136	−191	208	0	52	804	138	153
040	429	345	2,0,10	97	−94	806	272	223
042	121	117	2,0,12	128	−137	808	0	49
044	116	−146	301	376	−408	901	0	−63
046	208	−215	303	96	63	903	0	21
048	80	−70	305	383	288	905	0	33
0,4,10	68	100	307	303	245	907	0	52
051	103	−146	309	0	−57	10,0,0	148	188
053	253	−210	3,0,11	184	−173	10,0,2	0	61
055	86	−79	400	77	69	10,0,4	0	−82
057	113	94	402	0	−25	10,0,6	136	−131
059	125	131	404	0	2	11,0,1	102	128
060	220	−201	406	0	−10			

Table 5. *Unit-cell dimensions of* $BaHg_{11}$*-type compounds*

Compound	Cell dimension a (Å)	Cell volume V (Å^3)	Dx	Z	Formula weight
$RbHg_{11}$	9·734 ±0·002	922·3	12·38	3	2292·19
KHg_{11}	9·6455±0·0015	897·4	12·46	3	2245·81
$BaHg_{11}$	9·5852±0·0005	880·6	13·26	3	2344·07
$BaHg_{11}$*	9·60			3	
$SrHg_{11}$	9·5099±0·0008	860·1	13·29	3	2294·34

* Peyronel, 1952.

3·36 Å long. Mercury atoms in the connecting bond are in the acute angle in the parallelogram, and the connecting bond makes an angle of 157° with the parallelogram.

The mercury atoms in KHg_2 are in planar rectangular groups with 3·00 and 3·08 Å on edge. These rectangular groups share common edges to form a zigzag double atom chain. These chains are joined together by a Hg–Hg distance of 3·02 Å.

A better description of the structure results from its comparison to the $NaHg_2$ structure (the AlB_2 type) shown in Fig. 5. In the $NaHg_2$ structure, the mercury atoms form hexagonal layers, similar to the graphite layers. These mercury layers are stacked above one another in the hexagonal c direction. The Na atoms form a linear chain which fits into the hexagonal prismatic hole left by the mercury atoms. In the KHg_2

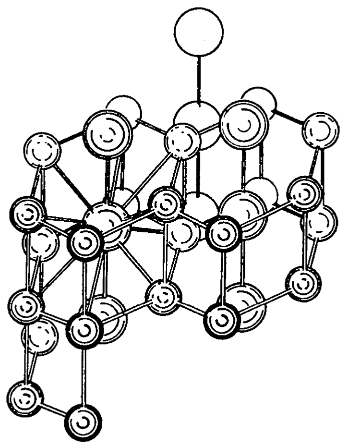

Fig. 5. The structure of $NaHg_2$. The small circles represent Hg atoms.

structure the K atoms are apparently too big for this arrangement. The Hg layers have been distorted, buckling in such a way that a slightly zigzag chain of K atoms can be accommodated in Na atom type holes.

As might be expected for intermetallic compounds which are exothermic upon formation, the interatomic distances between the atoms, particularly the K–K and K–Hg distances, are shorter by about 10% than the values calculated from the pure metals. In this way the K–Hg compounds are similar to the Na–Hg compounds reported previously.

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The Structure of Tussah Silk Fibroin*

(with a note on the structure of β-poly-L-alanine)

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A detailed structure for Tussah silk fibroin has been derived which is in agreement with the X-ray diffraction data. The structure is similar to that of *Bombyx mori* fibroin in that it is based on antiparallel-chain pleated sheets; the method of packing of the sheets, however, is quite different. This difference in packing can be explained on the basis of the chemical compositions of the two silks.

It seems highly probable that the structure of the β (stretched) form of poly-L-alanine is essentially that derived for Tussah silk.

Introduction

A detailed structure for commercial silk fibroin (*Bombyx mori*) has recently been formulated in these Laboratories (Marsh, Corey & Pauling, 1955). A prominent feature of the structure of *Bombyx mori* silk fibroin is the occurrence of glycine as alternate residues along the polypeptide chains.

Another form of silk fibroin is that derived from Tussah silk (commonly called wild silk). Previous investigators (Kratky & Kuriyama, 1931; Trogus & Hess, 1933) have shown that the X-ray diffraction pattern of Tussah silk fibroin, although having many features in common with the pattern obtained from *Bombyx mori*, is significantly different in several respects. Its chemical composition also differs from that of *Bombyx mori* in a very significant way (Table 1). The most striking differences are in the relative amounts of glycine and alanine. In particular, the amount of glycine in Tussah silk (26·6 residue %) is insufficient to permit the occurrence of glycine as alternate residues along the polypeptide chains. In

Table 1. *Composition of the fibroins of* Bombyx mori *and Tussah silks**

Amino-acid residue	*Bombyx mori* (residue %)	Tussah silk (residue %)
Glycine	44·4	26·6
Alanine	30·2	44·2
Serine	11·9	11·8
Tyrosine	4·9	4·9
Aspartic acid	1·4	4·7
Arginine	0·4	2·6
Valine	2·1	0·6
Glutamic acid	0·9	0·8
Tryptophan	0·2	1·1
Phenylalanine	0·6	0·5
Isoleucine	0·5	0·4
Leucine	0·5	0·4
Histidine	0·2	0·8
Proline	0·4	0·3
Threonine	1·0	0·1
Lysine	0·3	0·1
Cystine	0·1	—
Mean residue weight	78·3	83·5

* Calculated from the data of Schroeder & Kay (1955).

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