The Crystal Structures of Two Compounds Found in Dental Amalgam: Ag_2Hg_3 and Ag_3Sn*

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The structures of two of the three common compounds found in dental amalgam have been determined with single crystals. Intensity measurements were made with a diffractometer. The space group of Ag_3Sn is *Pmmn*; the cell constants (determined with powders and a diffractometer) are $a = 5.968$ (9), $b = 4.7802$ (4), $c = 5.1843$ (9) Å. There are two formula weights per cell. Close packed layers, each containing an ordered array of Ag and Sn atoms, occur at $b = \frac{1}{4}$ and $\frac{3}{4}$. No disorder was detected at temperatures below 175 °C. The weighted R value (on F) was 0.150. Ag_2Hg_3, although long considered to have the γ-brass structure (but with an unusual composition) is cubic with space group *I*23. The Hg atoms occupy general positions; vacancies of approximately 10% occur. There are 50 atoms per cell. The weighted R value (on F) was 0.187. Deformation markings are easily produced in Ag_3Sn. The shear elements are:

$$K_1 = (0\bar{1}0), \quad \eta_1 = [0\bar{1}\bar{1}];$$
$$K_2 = (011), \quad \eta_2 = [0\bar{1}1].$$

Intensity measurements from one such region indicate that the structure is the same as that of the unsheared crystal, indicating that these markings are true twins. Some growth twins were found in Ag_2Hg_3; the composition plane appears to be (112).

Introduction

Dental amalgam is a multi-phase solid consisting of the ε phase, Ag_3Sn, of the silver–tin system, the γ phase of the silver-mercury system, and the γ phase of the tin-mercury system. Some form of amalgam has been in use since about 1826 but the present form was first reported in 1895 (Black, 1895, 1896). A generalized equation for the amalgamation is given as (Ryge, Fairhurst & Fischer, 1961):

$$Ag_3Sn + Hg \rightarrow \gamma_1(Ag-Hg) + \gamma_2(Sn-Hg)$$
$$\text{unreacted } Ag_3Sn. \quad (1)$$
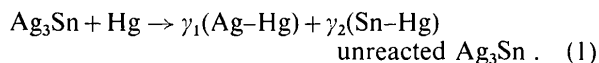
Previous studies (Fairhurst & Ryge, 1962) have identified and determined the structure of the Sn–Hg phase. The purpose of this investigation was to determine the crystal structures of the silver–tin and silver–mercury phases.

Murphy (1926) studied the equilibrium conditions of the silver–tin binary system and established the existence of Ag_3Sn. Preston (1926) described the structure as a close-packed hexagonal phase, but Hume-Rothery (1926) suggested that a multiple hexagonal cell would better satisfy the hexagonal symmetry and the composition requirements for Ag_3Sn. X-ray diffraction from powder specimens (Nial, Almin & Westgren, 1931) showed that the structure of Ag_3Sn was really a 'deformed' hexagonal close-packed structure; the orthorhombic lattice constants were reported as:

$$a = 2.98, b = 5.149, c = 4.771 \text{ Å}.$$

As all of this work was based on powder patterns the true structure could have been missed if any weak peaks were present. This condition exists for certain 'deformed' hexagonal structures (Karlsson, 1951).

The silver–mercury γ-phase was reported to be a body centered cubic structure (Murphy, 1931; Preston, 1931) with a cell edge of 10.0 Å. Berman & Harcourt (1938) examined natural crystals (which they called 'Moschellandsbergite') and assigned the *Im3m* space group to this mineral. Their chemical analysis of these crystals indicated the composition to be Ag_2Hg_3 and the density to be 13.48 g.cm^{-3}, in agreement with Murphy (1931).

Experimental

1. *Preparation of single crystals of* Ag_3Sn

Ag_3Sn crystals were obtained by slowly cooling melts containing 58 at.% tin from 525 to 300 °C (into the two-phase region Ag_3Sn plus liquid), then quenching the melts to 25 °C. The resulting ingots, containing about 50 vol.% of the Ag_3Sn phase, were then placed in concentrated HCl for twenty-four to forty-eight hours with intermittent cleansing in detergent solution in ultrasonic cleaning equipment. A large number of small crystals were freed from the ingot in this manner. The crystals were relatively ductile and mechanical deformation was readily produced. The deformation markings were detected with optical microscopy, and extra Bragg reflections occurred when they were present.

Care was taken to choose unmarked crystals for structural studies. Some crystallographic features of the deformation will be reported here.

2. Preparation of single crystals of Ag_3Hg_3

The silver-mercury γ-phase forms at $127\,^\circ$C by a peritectic reaction. Attempts to obtain suitable crystals from melts, or by diffusion anneals within the solubility limits of this phase, were unsuccessful. Crystals were obtained by slowly cooling melts containing 0·3 to 0·4 at.% silver in mercury. The melts were cooled from 110 to 30°C, through the liquid plus γ-phase region over a three-week period. The final temperature

was maintained for five days. The majority of the excess mercury was removed by aspirating through a linen cloth. The crystals were quite brittle and hence could be ground in a Bond (1951) crystal grinder. Although resulting shapes were nearly spherical, slight imperfections were still evident which can be important in structural studies for such highly absorbing elements as silver and mercury. Occasionally, twinned crystals were found.

3. X-ray techniques

The diffraction symbols were obtained with a precession camera. Many of the actual films have been

Table 1. *Values of hkl and* $\sin^2 \theta$ *for* Ag_3Sn, *copper K radiation* 25°C

Specimen was −325 mesh powder annealed in argon at 300°C for 15·5 hours. Slow scans on a diffractometer were employed; peak positions were determined by bisecting horizonal lines and extrapolating to the profile.
Wavelengths were those in *International Tables for X-ray Crystallography* (1962).

Parameter Standard deviation

$a = 5\cdot968$ Å $\quad$ 0·009 Å
$b = 4\cdot7802$ $\quad$ 0·0004
$c = 5\cdot1843$ $\quad$ 0·0009

hkl	λ	Calculated sin² θ	Observed sin² θ	hkl	λ	Calculated sin² θ	Observed sin² θ
002 c†	α	0·0885	0·0881	611	α_1	0·6504	0·6512*
020 b	α	0·1039	0·1035	243	α_1	0·6803	0·6789
012	α	0·1144	0·1142	440 a	α_1	0·6814	0·6811
022	α	0·1924	0·1920	440 a	α_2	0·6847	0·6844
312	α	0·2645	0·2636	523	α_1	0·7186	0·7200*
203	α	0·2653	0·2659	523	α_2	0·7221	
032	α_1	0·3218	0·3216	424	α_1	0·7233	0·7239*
223	α_1	0·3690	0·3676	621	α_1	0·7251	
104	α_1	0·3699	0·3696	424	α_2	0·7269	0·7262*
104	α_2	0·3717	0·3718	621	α_2	0·7287	0·7301*
014	α_1	0·3792	0·3785	334	α_1	0·7365	
412	α_1	0·3806	0·3806	052	α_1	0·7368	0·7367
014	α_2	0·3810	0·3816	334	α_2	0·7401	
330	α_1	0·3833	0·3836	051	α_2	0·7404	0·7404
040 b	α_1	0·4150	0·4149	044	α_1	0·7683	0·7680
040 b	α_2	0·4171	0·4169	044	α_2	0·7721	0·7716
024	α_1	0·4570	0·4566	006 c	α_1	0·7947	0·7949
422	α_1	0·4584		006	α_2	0·7987	
024 c	α_2	0·4592	0·4592*	350	α_1	0·7983	0·7981*
422	α_2	0·4607	0·4620*	603	α_1	0·7979	
304	α_1	0·5030		603	α_2	0·8019	
042	α_1	0·5033	0·5033	135	α_1	0·8020	0·8013*
304	α_2	0·5055		533	α_1	0·8483	
042	α_2	0·5058	0·5056	235	α_1	0·8520	0·8496
034	α_1	0·5867	0·5865	541	α_1	0·8533	
432	α_1	0·5881		631	α_1	0·8548	0·8543
034	α_2	0·5896	0·5892	235	α_2	0·8562	0·8558*
432	α_2	0·5910	0·5927	541	α_2	0·8575	0·8579*
503	α_1	0·6148	0·6159*	631	α_2	0·8590	0·8603*
404 a	α_1	0·6195	0·6192*	026 c	α_1	0·8985	0·8980
404 a	α_2	0·6226	0·6226*	623	α_1	0·9017	
513	α_1	0·6408	0·6418	026	α_2	0·9029	0·9026
414	α_1	0·6455	0·6459	623	α_2	0·9061	
414	α_2	0·6487		702	α_1	0·9039	0·9053*
530	α_1	0·6496	0·6485	702 a	α_2	0·9084	0·9097
530	α_2	0·6528		060 b	α_1	0·9338	0·9339
				060 b	α_2	0·9385	0·9385*

* Peaks were low in intensity and poorly defined.
† Peaks labeled *a*, *b*, *c* were used to obtain corresponding lattice constants by plotting against Nelson–Riley function =
$\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$.

reproduced elsewhere (Fairhurst, 1966). Integrated intensities were obtained by counting at discrete 2θ positions through a peak in a θ–2θ scan on a diffractometer. Care was taken to be sure the slits were open adequately to receive all of a peak, and the scan range was adjusted (for each peak) to be sure the background was reached. For Ag_3Sn, Rh-filtered Ag radiation was employed, to maximize the difference between the scattering of Ag and Sn atoms (which differ by only three in their atomic number). For Ag_2Hg_3, Mo radiation was employed, and when integrated intensities were obtained, balanced filters of Y and Zr were used, expect for very weak peaks for which only the Zr filter was used. Corrections were made for background in all cases, from readings on either side of a peak.

Patterson projections, electron density maps and least-squares refinement were performed on a CDC 3400 computer using Professor J. Ibers's mapping program ($FORDAP$) and a least-squares program (Busing, Martin & Levy, 1960) respectively. The variance $[\sigma^2(I)]$ of the intensity was calculated as (net counts)$^{-1}$; except for peaks less than sixteen times the minimum value for which, following Hughes (1941), $[16(\text{net counts})]^{-1}$ was employed.

Results

1. Ag_3Sn

Exposures on the precession camera of three to five days were employed so that any weak peaks whose intensity depended on the difference in scattering of Ag and Sn could be detected. Weak reflections were indeed found between rows of diffraction spots with constant h. From well annealed powders (see Table 1) the lattice parameters were found to be

$$a = 5\cdot968\ (9)\ \text{Å}$$
$$b = 4\cdot7802\ (4)$$
$$c = 5\cdot1843\ (9)$$

The a value is twice that previously reported (Nial et al., 1931).

The conditions for diffraction were:

$$(h00:\ h = 2n)\quad (hk0:\ h + k = 2n)$$
$$(0k0:\ k = 2n)$$

These conditions are consistent with either $Pm2_1n$ (or $P2_1mn$) $- C_{2v}^7$ (No. 31), and $Pmmn - D_{2h}^{13}$ (No. 59). On the basis of reported density values (Nial et al., 1931) and the new lattice parameters, the unit cell of Ag_3Sn contains eight atoms, six atoms of silver and two of tin. A trial model of the structure of Ag_3Sn was deduced from qualitative considerations of packing of a close-packed structure, plus the fact that the 200 reflection was relatively weak whereas the 400 was very strong. This structure has a packing efficiency 97% of that for a fully close-packed structure based on the metallic radii of Ag and Sn and the volume of the cell. The weak diffraction from the (200) planes can be accounted for by planes at $x = \frac{1}{4}$ and $x = \frac{3}{4}$ which contain all silver atoms, whereas the alternative planes might contain half silver and half tin. Attempts to pack such layers in the noncentrosymmetric space group yielded a value for the c axis twice the measured value. Distortions of the layers for $P2_1mn$ or $Pm2_1n$ seem unlikely in view of the close-packed nature of the structure. Furthermore, hkl peaks with h odd were quite weak, which would not be the case for the noncentrosymmetric space groups. The $Pmmn$ space group was therefore assumed to be the correct choice.

A crystal free of deformation markings, but possessing well-defined faces was chosen for collecting intensity data. (Its size was roughly 0·3 mm.) The Albrecht (1939) method was used to obtain absorption corrections, some 35,000 path-lengths being employed. One hundred and thirty-nine integrated intensities were measured and corrected.

From a ball model, trial atom parameters were

Table 2. *Parameters for* Ag_3Sn (*space group*: $Pmmn$, No. 59)

Origin at symmetry center
Thermal parameters β are multiplied by 10^4.

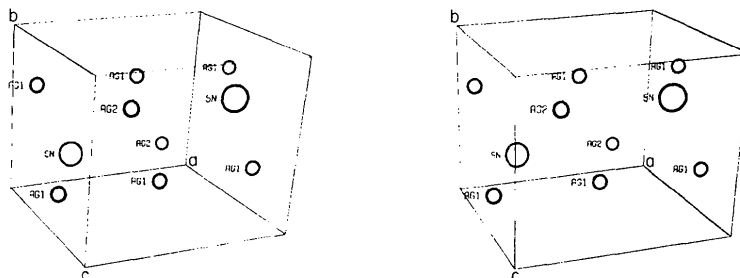|	Equipoint	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag_1	$4(f)$	0·00	$\frac{1}{4}$	$-0\cdot3369$ (7)	90 (10)	90 (20)	100 (10)	0	-77 (15)	0
Ag_2	$2(b)$	$\frac{1}{4}$	$\frac{3}{4}$	$-0\cdot1723$ (17)	110 (20)	47 (25)	127 (25)	0	0	0
Sn	$2(a)$	$\frac{1}{4}$	$\frac{1}{4}$	$0\cdot1687$ (13)	4 (10)	75 (25)	70 (14)	0	0	0

Fig. 1. Stereo pair of the unit cell of Ag_3Sn. [Drawn with $ORTEP$ (Johnson, 1965)].

obtained. Least-squares refinement was carried out calculating both the residual indices

$$R_1 = \frac{\sum_i (F_i^{obs} - F^{calc})}{\sum_i F_i^{obs}}$$

and

$$R_2 = \left[\frac{\sum_i w_i (F_i^{obs} - F_i^{calc})^2}{\sum_i w_i (F_i^{obs})^2} \right]^{\frac{1}{2}}$$

where w_i is a weight factor based on the variance of the measured intensities for each peak, $w_i = 1/\sigma(I)^2$. Refinement was on R_2. The scattering factors employed were those calculated by Cromer & Waber (1965) with corrections for anomalous scattering (Cromer, 1965). Anisotropic temperature factors were employed. Equivalent peaks were averaged; also some peaks (such as $h0l$ with h odd) which were only barely detected after long exposures on the precession camera, were not found with the relatively short times for the scans on the diffractometer. Some 55 reflections remained for the refinement.

The structure refined to an R_1 value of 0·109, using anisotropic thermal parameters and an R_2 of 0·150. Refinements with isotropic temperature factors gave $R_1 = 0·119$, $R_2 = 0·180$. The final parameters are given in Table 2, and the structure factors in Table 3. The structure is shown in Fig. 1. Some typical interatomic distances are given in Table 4.

Table 4. Characteristic distances in Ag_3Sn

Ag(1)–Ag(1) [56405]	2·928 Å*
Ag(1)–Ag(1) [55502]	2·984
Ag(1)–Ag(2) [55501]	2·944
Ag(1)–Ag(2) [56405]	2·950
Ag(1)–Sn [56505]	2·949
Ag(1)–Sn [55401]	2·966

* The first atom is in the first position of the rank 8 equipoint of $Pmmn$ (No. 59). Other positions are indicated as in $ORTEP$ (Johnson, 1965). The symbol in square brackets is:
$(5 + x$ unit cell translations) . $10^4 + (5 + y$ translations) . $10^3 + (5 + y$ translations) . $10^2 + ($number of coordinate set in general equipoint). The last value is the number of the coordinate set reading left to right in *International Tables for X-ray Crystallography* (1952).

Murphy (1926) reported a change in resistivity of Ag_3Sn at 60°C which might be due to disordering. Precession photographs were taken with Polaroid film, with the specimen heated by hot argon to 25, 105 and 175°C. No change in the weak reflections was observed.

2. Twinning in Ag_3Sn

Occasional deformation markings were first identified by two-surface analysis, measuring the angle between the two surfaces with an optical goniometer. [The surfaces were identified as (001) and (101) planes by diffraction.] The plane of the markings (K_1) was (0$\bar{1}$1). The tilt between the (001) face and a marking was 5·5° and that between a marking and the (101) face was 5·3°. With these tilts, a stereographic analysis was performed assuming the marking was due to simple shear, to obtain the shear direction (η_1) (Greninger & Troiano, 1949). η_1 was [0$\bar{1}$1]. Precession photographs of crystals with markings were taken of the (100)* plane which is parallel to the 'plane of shear' – the plane perpendicular to K_1 and containing η_1. As many as twenty extra spots were observed, all of which were reflections (across the trace of K_1 in this plane) of spots in crystals without markings. This strongly suggested that the specimen was twinned. Accordingly, by trial and error the second undistorted plane in a simple shear (K_2) was located. The trace of this plane in K_1 must be perpendicular to η_1 and its position before and after shear must be symmetrically located with respect to the normal to K_1. Furthermore, as η_1 and K_1 are rational, K_2 must be as well (Cahn, 1954). One plane that satisfied these conditions was (011). η_2, the second undistorted line, must lie in K_2 and be perpendicular to the line of intersection of K_2 and K_1; η_2 is then [0$\bar{1}$1]. The shear (s) is:

$$s = 2 \cot 85·2° = 0·168$$

where 85·2° is the angle between K_1 and K_2. The shearing process is indicated by Fig. 2 from which it can be seen that:

Table 3. Observed and calculated structure factors for Ag_3Sn

K	L	FO	FC
***** H = 0 *****			
0	2	6519	8882
0	4	4943	5686
0	5	2232	1045
0	6	6714	7110
0	8	2390	2212
0	10	1237	1283
0	12	1127	1419
1	1	713	538
2	0	19053	17456
2	2	9369	7433
3	3	599	741
4	0	11083	11351
4	4	5281	3875
6	0	8219	7447
6	6	4873	4124
8	0	5233	4933
8	8	1501	1013
10	0	3013	3160
12	0	1595	1886
***** H = 1 *****			
0	1	383	389
0	2	533	606
0	5	532	493
***** H = 2 *****			
0	0	483	454
0	1	8113	8859
0	2	755	834
0	3	11994	12990
0	4	709	639
0	5	4971	4270
0	7	2882	2689
0	8	707	752
2	0	486	517
***** H = 3 *****			
0	1	433	407
0	2	447	428
3	0	499	522
***** H = 4 *****			
0	0	11441	13045
0	2	6542	5809
0	3	551	545
0	4	4518	4296
0	6	6078	5965
0	8	1829	1950
0	10	1370	1232
4	0	9166	8595
***** H = 6 *****			
0	2	747	697
0	3	7685	7439
0	9	2753	2794
***** H = 8 *****			
0	0	6698	6073
0	2	3463	2892
0	4	2432	2456
0	6	4098	3929
0	8	1541	1406
0	12	1261	1238
8	0	3119	2618
***** H = 10 *****			
0	5	1348	1679
***** H = 12 *****			
0	0	2990	2981
0	6	2012	2250

(100) Projection

(a)

(b)
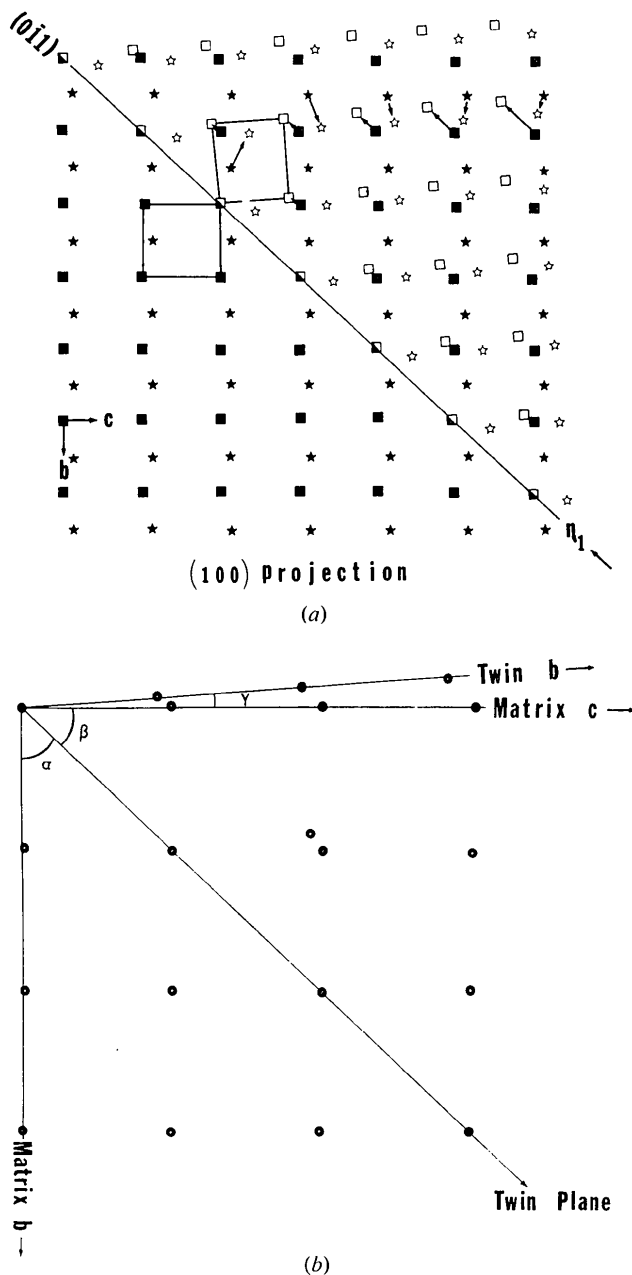
Fig. 2. (a). Relative positions of atoms before and after twinning in Ag₃Sn. Stars are Ag atoms, squares are Sn. Arrows indicate total movement of atoms. Initial positions prior to shear and shuffles are indicated by filled symbols. Final positions are open symbols. (b) Plane of shear; unit cell corners indicated by dots. The angles γ, α, β are shown.

(a) atoms must 'shuffle' in directions other than the shear direction if the product is to be a twin. Otherwise a new structure is generated by the shear, with b and c axes interchanged. Intensity data for 002, 004, 006, 020, 040, 060 from an untwinned crystal and a twinned crystal agreed; particularly the 006 was similar in intensity to the 004, whereas the 060 was much weaker than the 040. If no 'shuffles' had occurred the 060 would be similar in intensity to the 040, but the 006 would be much less in intensity than the 004. [see Fig. 2(a).]. The structure within a deformation marking is a twin.

(b) A simple check that K_2 was correctly chosen can be obtained by measuring the angle γ [Fig. 2(b)] between diffraction from 00l in a crystal and 0k0 in its twin; with the known cell constants the angle γ was calculated to be 4·4°. The measured angle was 4·7°. It is somewhat surprising that twinning and not a new structure is generated by shear, in view of the fact that large 'shuffles' are involved to maintain the ordered arrangement. It has been predicted in such cases that a new structure is expected (Laves, 1952). However, it is worth pointing out in this regard that simple shears in the **b** and **c** directions on a hard sphere model will carry out the entire atomic rearrangement without shuffles (Fairhurst, 1966).

In the Introduction it was pointed out that the unit cell is pseudo-hexagonal. In hexagonal indices, the twin plane is (10$\overline{1}$2) which is a common K_2 for twinning in hexagonal metals (Rosenbaum, 1964). K_2 in Ag₃Sn is K_1 in hexagonal metals. The magnitude of the shear is also comparable. η_1 and η_2 are not, however, equivalent.

3. Ag₂Hg₃

Precession photographs taken at 90° intervals around $\langle 100 \rangle$ axes confirmed that the structure is cubic. The symmetry of the cube axis was twofold; thus, the Laue symmetry was $m3$. Extinctions were found only for $h+k+l = $ odd. There were four possible space groups: $I23 - T^3$ (No. 197), $I2_13 - T^5$ (No. 199), $Im3 - T_h^5$ (No. 204), and $Ia3 - T_h^7$ (No. 206). The $Ia3$ space group could be eliminated as the reflections observed included 013, 017, 015, etc., which are not allowable in this case. The chemical analysis of this phase, as indicated by Murphy (1931) suggests the compound is Ag₂Hg₃. The density was reported as 13·48 g.cm⁻³. Using a lattice parameter of 10·0 Å, the number of atoms per unit cell is about fifty.

Intensities from the near-spherical crystal corrected

Table 5. *Structural parameters* ($\times 10^4$) *for* Ag₂Hg₃ (*space group: I23 No. 197*)

	Equi-point	Occupation factor	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
								Temperature factors			
Hg₁	(c)	8	1151 (7)	1151	1151	38 (5)	38	38	6 (5)	6	6
Ag₁	(c)	8	3285 (10)	3285	3285	9 (5)	9	9	3 (6)	3	3
Hg₂	(f)	22·2 (1·1)	2957 (6)	3359 (7)	291 (6)	16 (4)	50 (6)	23 (5)	−4 (4)	−5 (3)	−11 (4)
Ag₂	(d)	12	3550 (15)	0	0	23 (10)	32 (10)	17 (9)	0	0	3 (12)

for absorption* were used to prepare a three-dimensional Patterson function. The sections containing significant Patterson peaks were $z = 0.0$, 0.175, 0.325. For $I2_13$ there are not proper equipoints to distribute the 30 atoms of Hg and 20 atoms of Ag to obtain an ordered structure. For ordered structures in $Im3$ and $I23$ the 20 Ag atoms must be distributed in such a way that vectors at $\frac{1}{2}, \frac{1}{2}, 0$ or $\frac{1}{2}, 0, 0$ are required in the Patterson synthesis. These were absent.

It has long been thought that this material was a γ-brass type in view of the large cubic cell and the electron-to-atom ratio of 1·6. Many of these compounds contain 52 atoms in a unit cell, but it is not unusual for such structures to have vacant sites (Betterton & Hume-Rothery, 1952). Hence, the possible space groups were reconsidered with 32 Hg sites per cell, two of which are vacant and chosen at random from cell to cell. (If 22 Ag and 30 Hg atoms are considered, reasoning similar to that in the previous paragraph eliminates this possibility.) $I2_13$ and $Im3$ were still not possible. The only possible space group was $I23$ with Hg atoms on $24(f)$ and $8(c)$ equipoints and Ag on $12(d)$ and $8(c)$. The atomic coordinates are:

$$(0,0,0; \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) +$$

$24(f)$: $x,y,z; z,x,y; y,z,x; x,\bar{y},\bar{z}; z,\bar{x},\bar{y}; y,\bar{z},\bar{x}$
$\bar{x},y,\bar{z}; \bar{z},x,\bar{y}; \bar{y},z,\bar{x}; \bar{x},\bar{y},z; \bar{z},\bar{x},y; \bar{y},\bar{z},x$

$12(d)$: $x,0,0; 0,x,0; 0,0,x; \bar{x},0,0; 0,\bar{x},0; 0,0,\bar{x}$

$8(c)$: $x,x,x; x,\bar{x},\bar{x}; \bar{x},x,\bar{x}; \bar{x},\bar{x},x$.

$I\bar{4}3m - T_d^3$ (No. 217), the space group for the structure having the *Strukturbericht* designation $D8_2(Cu_5Zn_8)$, is a typical γ-brass type. The rank 24 equipoint in this case has the form xxz rather than xyz for $I23$. Both groups are noncentrosymmetric. The 411 and 330 peaks are strong reflections from Ag₂Hg₃ as for the known $D8_2$ structures. For all these reasons, it was decided to refine the structure using as starting parameters atomic coordinates for Cu_5Cd_8 (Bradley & Gregory, 1931). Again atomic scattering factors were corrected for dispersion (Cromer, 1965; Cromer & Waber, 1965).

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* μr was taken to be 14, by averaging the radius at several points, and the corrections for a sphere in *International Tables for X-ray Crystallography* (1959) were employed.

After initial stages of refinement, equivalent reflections were averaged and those that had intensities less than three standard deviations were eliminated, reducing the number of independent reflections from 231 to 160. Refinement was continued with isotropic and anisotropic temperature factors. In both cases, the occupation of the Hg $24(f)$ equipoint was a variable. With anisotropic factors R_1 was 0.143, R_2 was 0.187; for isotropic temperature factors, $R_1 = 0.160$, $R_2 = 0.208$. Results are given in Table 5 for the anisotropic factors, and the structure factors are given in Table 6. Note that there are about two vacant Hg sites on the rank 24 equipoint; with the error on this value it is barely significant, but is supported by the reported density and lattice parameter; as mentioned earlier, these lead to 50 atoms per cell.

[Baird & Muller (1969a) have attempted to refine our data using an orthorhombic structure but found that the resulting parameters were cubic, further sup-

Table 6. *Observed and calculated structure factors for Ag_3Hg_3*

[Structure factor table with columns H, L, FO, FC grouped by K values — dense numerical data omitted for fidelity]

Fig. 3. Stereo pair of the unit cell of Ag₃Hg₃. [Drawn with *ORTEP* (Johnson, 1965)]. Large atoms are Hg. Two of these sites are vacant in the structure.

porting the space group we have chosen. They also tried a least-squares refinement for the cubic space group used here, *I*23, but used only unit weighting, no corrections for anomalous dispersion, and also appear to have chosen the wrong equivalences (due to symmetry) of the anisotropic temperature factor for the Ag atoms on the 12(*d*) equipoint.]

The unit cell is shown in Fig. 3. The lattice parameter employed was 10·0506 Å for Hg-rich Ag_2Hg_3 (Dreiner, 1958). Some typical interatomic distances are given in Table 7.

Table 7. *Nearest-neighbor distances in* Ag_2Hg_3

Hg(1)–Hg(1) [55504]	3·272 Å*
Hg(2)–Hg(2) [55521]	2·936
Hg(1)–Hg(2) [55501]	2·994
Hg(1)–Ag(1) [45516]	2·990
Hg(1)–Ag(2) [55501]	2·914
Hg(2)–Ag(1) [55422]	2·890
Hg(2)–Ag(2) [55518]	2·880
Ag(1)–Ag(2) [55517]	3·057
Ag(2)–Ag(2) [65507]	2·915

* The first atom is in the first position of the equipoint. The second position is indicated as in *ORTEP* (Johnson, 1965). The symbol represents $(5+x$ unit cell translations) . $10^4 + (5 + y$ translations) . $10^3 + (5 + z$ translations) . $10^2 + $ (number of coordinate set in general equipoint). The last term is obtained by counting from left to right in the positions given in the text.

There are two interesting features of this structure: (i) The majority of the heavy mercury atoms are in general positions. The result of this is that the structure has only twofold symmetry along the cube axis instead of the fourfold in the $D8_2$ structures of Cu_5Zn_8 and Cu_5Cd_8; (ii) the total electron count for all the atoms in the cell is about 76, lower than the values of 84–88 usually found for such compounds. (It should be kept in mind that the crystals were prepared from Hg-rich solid solutions, so that the electron count would be the highest over the range of compositions for which this phase exists.)

4. Twinning in Ag_2Hg_3

Some extra reflections were found for certain crystals grown at room temperature, which appeared to be reflections of other spots across (112) planes. A similar twinning has been detected by Baird & Muller (1969b) in crystals grown from nitrate solutions.

Discussion

A new unit cell was detected for Ag_3Sn. The structure is ordered and remains so until at least 175°C. This phase deforms mechanically, and intensity data show that observed shear markings are true twins, despite the ordered arrangement of atoms. The structure can be described as deformed hexagonal similar to structures with the *Strukturbericht* designation DO_{22}. It has the same structure as Cu_3Ti (Laves & Walbaum, 1939; Karlson, 1951), and Mo_3Ni (Saito & Beck, 1959). In

all these phases nearly close-packed layers are stacked along a pseudo threefold axis (the *b* axis), in a h.c.p. sequence, *abab* .... The layers themselves consist of ⟨100⟩ rows of atoms, alternating rows being all Ag or half Ag–half Sn, as can be seen in Fig. 1. It is interesting to note that all of these phases reported previously have involved one or more transition elements, whereas Ag_3Sn does not. The pseudo-hexagonal nature of the structure also expresses itself in its twinning mode, which is similar to that for hexagonal metals.

The similarity of the structure of Ag_2Hg_3 to that of the γ-brass type, $D8_2$, has already been pointed out. The reduced symmetry of the general position as compared to $D8_2$ may be due to the vacant sites in the structure of Ag_2Hg_3.

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The Crystal Structure of 4-Carbethoxyanilinium Bis-*p*-nitrophenylphosphate

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The crystal structure of a 1:1 complex between 4-aminobenzoic acid ethyl ester and bis-*p*-nitrophenylphosphate has been determined. Crystals are orthorhombic, $Pna2_1$, $a = 12.273$ (4), $b = 27.357$ (4), $c = 7.114$ (4) Å, $Z = 4$. The intensities of 2221 reflections were measured with a four-circle automated diffractometer using Cu $K\alpha$ radiation. The structure was refined to an R of 0.049 over all the reflections. In the complex the 4-amino group is protonated. All three of the amino hydrogen atoms participate in hydrogen bonds to the phosphate group with N---O distances of 2.754, 2.780, and 2.838 Å. The bis-*p*-nitrophenylphosphate ion, which is also found in crystalline complexes with phenacaine and procaine, has a CO–P–OC valency angle of 97.8°. This structural feature, along with the torsion angles about the phosphate ester bonds, shows greater similarity to that in the phenacaine complex. The molecular packing indicates that the nonpolar interactions between the components of the complex are more extensive than was observed in the procaine complex. This aspect was also apparent in the structure of the phenacaine complex, although not to the same extent as in the present structure.

Introduction

On the basis of studies with model systems (Feinstein, 1964; Feinstein & Paimre, 1966), Feinstein and Paimre suggested that local anesthetics block nerve conduction by complexing with phospholipids in the neural membrane. Their studies demonstrated that the local anesthetics would precipitate phospholipids or phosphodiester compounds in general. In fact, the reaction with a simple phosphodiester, bis-*p*-nitrophenylphosphate, resulted in the precipitation of a crystalline complex. To examine the nature of this interaction, we determined the crystal structures of several of these complexes (Sax, Pletcher & Gustaffson, 1970; Sax, Pletcher, Yoo & Stewart, 1971). The results of these structure analyses, along with other experimental observations, led to the suggestion that the hydrogen-bond donor capability of local anesthetics was an

important aspect in the anesthetics' mode of action (Sax & Pletcher, 1969). In exploring this idea further, we attempted to prepare a complex with a neutral, nonionizable local anesthetic. Benzocaine, which is 4-aminobenzoic acid ethyl ester, was selected for this purpose as it is normally regarded as a neutral, nonionizable drug. Contrary to expectation that the benzocaine complex with bis-*p*-nitrophenylphosphoric acid would exist in the uncharged or neutral form, crystal-structure analysis shows that the complex crystallizes in the ionized form.

Experimental

Crystals of the complex were prepared by mixing equimolar solutions of bis-*p*-nitrophenylphosphoric acid* and benzocaine† in absolute methanol. White needle-shaped crystals of the complex were obtained

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* Aldrich Chemical Company.
† Eastman Organic Chemicals.