The Crystal Structure of \( \text{Au}_6\text{Hg}_8 \)

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The phase \( \text{Au}_6\text{Hg}_8 \) has been synthesized at 25°C and 80°C. The structure has been determined and refined by least-squares techniques on the basis of three-dimensional X-ray single crystal data. The dimensions of the hexagonal unit cell are:

\[
\begin{align*}
\alpha &= 6.9937 \pm 2 \text{ Å} \quad \text{and} \quad c = 10.1480 \pm 4 \text{ Å in equilibrium with liquid mercury and} \\
\alpha &= 6.9838 \pm 2 \text{ Å} \quad \text{and} \quad c = 10.1510 \pm 5 \text{ Å in equilibrium with Au}_4\text{Hg}. \text{ The space group is P6}_3/mcm \text{ and gold is positioned in 12(k) (x=0.2416,} \\
&\quad z=0.3902) \text{ and mercury in 6(g) (x=0.3884) and 4(d).}
\end{align*}
\]

Previous crystallographic investigations of the Au-Hg system by Pabst,\(^1\) Stenbeck,\(^2\) and Plaksin\(^3\) all agree on the existence of a hexagonal close-packed phase with the ideal composition \( \text{Au}_6\text{Hg}_8 \). With higher mercury content, phases of unknown symmetry and compositions around \( \text{Au}_2\text{Hg}_3 \)\(^1\) and \( \text{AuHg}_2 \)\(^1,3\) have been suggested.

In this work a hexagonal phase with the composition \( \text{Au}_6\text{Hg}_8 \) has been found to form in equilibrium with \( \text{Au}_4\text{Hg} \) and also with Hg(1) at 80°C. This is in agreement with the observations of Winterhager and Schlesser \(^4\) as the X-ray diffraction pattern obtained from the final product in their measurements of diffusion of mercury in gold may be indexed on the basis of a hexagonal cell with \( \alpha = 6.95 \pm 1 \text{ Å} \) and \( c = 10.10 \pm 6 \text{ Å} \) (calculated from \( d \)-values given with two decimals).

EXPERIMENTAL

Samples for phase analysis were prepared by reduction of metal ions with hydrazine sulfate (\textit{pro analysis}, Merck) in ammoniacal solutions at 80°C according to Kulifay.\(^4\) Weighed amounts of gold (tubing, 99.9 %) dissolved in aqua regia and mercuric oxide (\textit{pro analysis}, Merck) dissolved in nitric acid were thoroughly mixed together, added to the reducing solution and allowed to stand on a hot water rack for one hour to sediment. The reduction was found to be almost quantitative, and all compositions reported in the text and in the tables are synthetic. Only in the samples with a large excess of liquid mercury could individual crystals be detected with the microscope. Single crystals of \( \text{Au}_6\text{Hg}_8 \) were prepared electrolytically with a mercury cathode and a gold anode in an electrolyte of dilute hydrochloric acid. The sample was allowed to recrystallize at room...
CRYSTAL STRUCTURE OF Au₄Hg₄

temperature for three months before the excess of mercury was removed by careful etching with nitric acid. Regular crystals with dimensions of up to 0.8 mm were thus obtained.

X-Ray powder diffractograms of all preparations were taken in a Guinier camera with strictly monochromatized CuKα₁ radiation, λ = 1.54050 Å, and with KCl, a = 6.2919 Å (20°C) as an internal standard. The density of Au₄Hg₄ was determined by weighing of the electrolytically prepared sample in air and in bromobenzene.

Single crystal X-ray data of Au₄Hg₄ have been collected with a General Electric Diffractometer equipped with a quarter-circle single crystal orienter and a scintillation counter. Nickel filtered CuKα₁ radiation, with pulse height discrimination was used for the intensity measurements. Pulses were counted for 40 sec during a θ – 2θ scan across each diffraction peak. One octant of the reciprocal lattice was measured with regular checks in other octants for determination of the symmetry elements.

The crystal was a regular hexagonal prism with pyramids on both ends and with a fairly uniform diameter of 0.04 mm. Its shape was determined under the microscope and the equations of the 18 surfaces were used for correction of the intensities for absorption (μ = 3380 cm⁻¹) by approximate numerical integration. The 210 measured reflexions were then converted to 122 independent structure factors. Atomic scattering factors were taken from Cromer and Waber’s (corrected for dispersion according to Cromer’s). Full matrix least-squares refinement of the atomic positional and thermal parameters was carried out on an IBM 360/75 computer with the program LALS (Word list No. 384) in which an individual weighting w = 1/σ² was used. σ was obtained from counter statistics.

PHASE ANALYSIS

In Table 1 are listed the phases observed in the various Au₄Hg₁₀₀₋ₓ preparations together with the lattice parameters of the hexagonal cells. The cell dimensions of Au₄Hg are in agreement with earlier reports.

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Au₄Hg₄ would be homogeneous at x = 54.55, but a few weak lines from Au₄Hg are still present in the powder pattern of x = 54 possibly due to synthetic errors or some equilibrium failure. The presence of liquid mercury has been detected under the microscope by careful pressing of a sample under a piece of transparent cello-tape. No attempt to determine the homogeneity range at the mercury-rich side of Au₄Hg₄ has been made since it would be very difficult to detect small amounts of liquid mercury in the samples. The indexing of Au₄Hg₄ is presented in Table 2.

Table 2. Guinier powder pattern of Au$_2$Hg$_4$. \( a = 6.9937 \pm 2 \) Å, \( c = 10.1480 \pm 4 \) Å. Hexagonal indexing.

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STRUCTURE DETERMINATION

The intensity distribution indicated the crystal class to be \( 6mm \) or \( 6/mmm \). Systematic absences of \( hhl \) reflections for \( l = 2n + 1 \) gave two possible space groups viz. \( P6_3cm \) (No. 185) and \( P6_3/mcm \) (No. 193). An interpolation among

the mean atomic volumes for Au (16.9 Å³), Au₃Hg (17.5 Å³), and Hg (23.4 Å³) to a composition Au₅₄Hg₄⁶ gives a mean atomic volume of about 18.3 Å³, and a content of 22 atoms within one unit cell. The observed density was 16.3 g cm⁻³ and a calculated density for Au₁₂₅Hg₁₀ is 16.875 g cm⁻³.

Possible packing maps of layers perpendicular to the c-axis were constructed for atoms of 3 Å diameter with respect to the symmetry elements involved in the two space groups. Owing to the dimensions of the a-axis it became evident that only positions such as x,0,z, 1/3, 2/3,z, and 0,0,0 were possible. Just a few plausible crystal models can be obtained by the stacking of such layers in the z-direction. Least-squares refinements of positional and thermal parameters using a mercury scattering factor table for all atoms were performed in space group P6₃mc for those models. One model was superior in all respects to the others and converged to an R-value of 7.6 % (unweighted).

A comparison of the interatomic distances in that model with those in the solid solution of mercury in gold¹ (2.88—2.90 Å) and in mercury metal (3.005 and 3.470 Å) showed that a centro-symmetrical arrangement of the gold atoms in a 12-fold position would relate the shortest distances to Au—Au and Au—Hg contacts and the longer distances to Hg—Hg contacts. As the numerical

Table 3. Observed and calculated structure factors for Au₅₄Hg₄⁶. R=7.6 %.

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values of the positional parameters were not far from those of a centrosymmetric model another run was performed in space group \( P6_3/mcm \). This refinement ended with \( R=7.6 \% \) (unweighted) and \( R=7.5 \% \) (weighted). The conservation of the \( R \)-value and the plausible interatomic distances thus obtained may justify the selection of \( P6_3/mcm \) as the correct space group. No further improvement could be attained by introduction of separate scattering factors for gold and mercury.

Table 4. Interatomic distances with coordination number and standard deviations.

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<td>Hg(1)</td>
<td>6</td>
<td>3.298</td>
<td>Å</td>
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Final positional and thermal parameters were:

12\( k \) Au \( x = 0.2416 \pm 5, y = 0, z = 0.3902 \pm 4, B = 0.52 \pm 9 \, \text{Å}^2 \)

6\( g \) Hg(1) \( x = 0.5864 \pm 7, y = 0, z = 1/4, B = 0.63 \pm 11 \, \text{Å}^2 \)

4\( d \) Hg(2) \( x = 1/3, y = 2/3, z = 0, B = 0.62 \pm 12 \, \text{Å}^2 \)

Observed and calculated structure factors are presented in Table 3 and interatomic distances in Table 4.

The structure may be described in terms of 10-coordination polyhedra around Hg(1). One polyhedron and the packing of one layer of polyhedra

![Figure 1](image.png)

Fig. 1. The 10-coordination polyhedron around Hg(1) and one layer of polyhedra projected along the c-axis.

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CRYSTAL STRUCTURE OF \( \text{Au}_4\text{Hg}_6 \)

projected along the \( c \)-axis are shown in Fig. 1. The next layer is rotated 60° around the \( c \)-axis and displaced \( c/2 \). The polyhedra of the upper layer share the \( \text{Hg}(2) - \text{Hg}(2) \) edges with the lower layer.

The 12-coordination around \( \text{Hg}(2) \) is somewhat related to the packing in mercury metal. One 12-coordination polyhedron and its projection along the \( c \)-axis is presented in Fig. 2. There are three \( \text{Hg}(1) \) above and three below at a distance of 3.298 \( \text{Å} \) and an irregular staggered 6-membered ring of gold at a distance of 2.930 \( \text{Å} \). In mercury metal the corresponding distances are 2.999 \( \text{Å} \) and 3.463 \( \text{Å} \).

![Fig. 2](image)

Fig. 2. The 12-coordination polyhedron around \( \text{Hg}(2) \) and its projection in the \( c \)-direction.

The structure may also be described with the 12-coordination polyhedron around \( \text{Hg}(2) \). This polyhedron appears in two enantiomorphous forms separated by the mirror planes. One polyhedron will thus be surrounded by five polyhedra of the other form viz. three in the same \( a - a \) plane sharing the \( \text{Au} - \text{Hg}(1) - \text{Au} - \text{Hg}(1) \) parallelograms and one on each side along the threefold axis sharing the regular \( \text{Hg}(1) - \text{Hg}(1) - \text{Hg}(1) \) triangular surfaces.

As the 10- and 12-coordination polyhedra might be unique to this structure templates for three dimensional model constructions are shown in Figs. 3 and 4. In these figures there are also some interatomic distances presented in \( \text{Å} \).

![Fig. 3](image)

Fig. 3. Template for construction of the 10-coordination polyhedron around \( \text{Hg}(1) \).

![Fig. 4](image)

Fig. 4. Template for construction of the 12-coordination polyhedron around \( \text{Hg}(2) \).

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Crystals of Au₄Hg₅ are brittle with the same colour as mercury. When they are heated in air under the microscope a visible loss of mercury starts at about 70°C. D.T.A. investigations carried out with heating of samples in closed evacuated silica capsules indicate a reversible endothermic process at 132—140°C and at temperatures above 200°C there is a slow exothermic reaction. No melting point could be detected for a sample heated to 600°C. The powder pattern from that sample was very complex and had no lines of Au, Au₄Hg, or Au₄Hg₅, thus indicating the presence of at least one additional phase in the system. An investigation at higher temperatures is in progress.

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REFERENCES


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