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The Crystal Structure of Au_6Hg_5

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The phase Au_6Hg_5 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:
$a=6.9937\pm2$ Å and $c=10.1480\pm4$ Å in equilibrium with liquid mercury and
$a=6.9838\pm2$ Å and $c=10.1510\pm5$ Å in equilibrium with Au_3Hg. The space group is $P6_3/mcm$ and gold is positioned in 12(k) ($x=0.2416$, $z=0.3902$) and mercury in 6(g) ($x=0.5864$) and 4(d).

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 Au_3Hg. With higher mercury content, phases of unknown symmetry and compositions around Au_2Hg_3 [1] and $AuHg_2$ [1,3] have been suggested.

In this work a hexagonal phase with the composition Au_6Hg_5 has been found to form in equilibrium with Au_3Hg and also with Hg(l) at 80°C. This is in agreement with the observations of Winterhager and Schlosser [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 $a=6.95\pm1$ Å and $c=10.10\pm6$ Å (calculated from d-values given with two decimals).

EXPERIMENTAL

Samples for phase analysis were prepared by reduction of metal ions with hydrazine sulfate (*pro analysi*, Merck) in ammoniacalic solutions at 80°C according to Kulifay.[5] Weighed amounts of gold (tubing, 99.9 %) dissolved in aqua regia and mercuric oxide (*pro analysi*, 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 Au_6Hg_5 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

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 Cu$K\alpha_1$ radiation, $\lambda = 1.54050$ Å, and with KCl, $a = 6.2919$ Å (20°C) as an internal standard. The density of Au_6Hg_5 was determined by weighing of the electrolytically prepared sample in air and in bromobenzene.

Single crystal X-ray data of Au_6Hg_5 have been collected with a General Electric Diffractometer equipped with a quarter-circle single crystal orienter and a scintillation counter. Nickel filtered Cu$K\alpha$ radiation, with pulse height discrimination was used for the intensity measurements. Pulses were counted for 40 sec during a $\theta - 2\theta$ 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 ($\mu = 3390$ cm^{-1}) by approximate numerical integration. The 210 measured reflexions were then converted to 122 independent structure factors. Atomic scattering factors was taken from Cromer and Waber [6] (corrected for dispersion according to Cromer [7]). 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 [8] No. 384) in which an individual weighting $w = 1/\sigma^2$ was used. σ was obtained from counter statistics.

PHASE ANALYSIS

In Table 1 are listed the phases observed in the various Au_xHg_{100-x} preparations together with the lattice parameters of the hexagonal cells. The cell dimensions of Au_3Hg are in agreement with earlier reports.

Table 1. Phases observed in preparations at 80°C of synthetic composition Au_xHg_{100-x}. Lattice parameters are given for Au_3Hg and Au_6Hg_5.

		Au_3Hg		Au_6Hg_5	
x	Phases	a Å	c Å	a Å	c Å
80	$Au + Au_3Hg$	2.9095 ± 3	4.7896 ± 2		
70	$Au_3Hg + Au_6Hg_5$				
60	$Au_3Hg + Au_6Hg_5$	2.9190 ± 2	4.8105 ± 4	6.9838 ± 2	10.1510 ± 5
55	$Au_3Hg + Au_6Hg_5$				
54	$(Au_3Hg) + Au_6Hg_5$				
50	$Au_6Hg_5 + Hg(l)$				
40	$Au_6Hg_5 + Hg(l)$			6.9937 ± 2	10.1480 ± 4

Au_6Hg_5 would be homogeneous at $x = 54.55$, but a few weak lines from Au_3Hg 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 Au_6Hg_5 has been made since it would be very difficult to detect small amounts of liquid mercury in the samples. The indexing of Au_6Hg_5 is presented in Table 2.

Table 2. Guinier powder pattern of Au_4Hg_5. $a = 6.9937 \pm 2$ Å, $c = 10.1480 \pm 4$ Å. Hexagonal indexing.

I	$h\,k\,l$	$\sin^2\theta_{obs}$	$\sin^2\theta_{cal}$	$10^5 \times \Delta\sin^2\theta$
w	1 0 0	0.01611	0.01617	−6
w	1 1 0	0.04849	0.04851	−2
w	1 1 1	0.05432	0.05427	5
w	2 0 0	0.06461	0.06469	−8
s	1 1 2	0.07155	0.07156	−1
s	2 0 2	0.08776	0.08773	3
vs	1 1 3	0.10052	0.10036	16
s	1 0 4	0.10844	0.10834	10
m	2 1 0	0.11324	0.11320	4
vs	2 1 1	0.11901	0.11896	5
w	2 1 2	0.13621	0.13625	−4
m	1 1 4	0.14075	0.14069	6
m	3 0 0	0.14566	0.14555	11
m	2 0 4	0.15687	0.15686	1
m	2 1 3	0.16511	0.16505	6
w	3 0 2	0.16856	0.16859	−3
m	1 1 5	0.19258	0.19254	4
vw	2 2 1	0.19994	0.19983	11
vw	2 1 4	0.20547	0.20538	9
w	0 0 6	0.20750	0.20739	11
w	3 1 1	0.21604	0.21600	4
vw	1 0 6	0.22366	0.22357	9
vw	3 0 4	0.23769	0.23773	−4
s	1 1 6	0.25593	0.25591	2
w	4 0 0	0.25894	0.25876	18
m	3 1 3	0.26213	0.26209	4
vw	2 0 6	0.27221	0.27208	13
m	2 2 4	0.28619	0.28624	−5
s	3 1 4	0.30251	0.30242	9
w	3 2 1	0.31302	0.31304	−2
m	3 2 2	0.33051	0.33032	19
	1 1 7		0.33081	
m	4 1 0	0.33967	0.33962	5
s	4 0 4	0.35110	0.35093	17
w	3 1 5	0.35439	0.35427	12
w	4 1 2	0.36279	0.36267	12
m	0 0 8	0.36858	0.36870	−12
vs	2 1 7	0.39552	0.39550	2
w	3 2 4	0.39950	0.39945	5
w	2 2 6	0.40147	0.40147	0
w	5 0 0	0.40405	0.40431	−26
w	5 0 2	0.42743	0.42736	7
w	3 3 1	0.44245	0.44242	3
w	4 2 0	0.45253	0.45283	−30
w	4 0 6	0.46607	0.46616	−9
w	2 1 8	0.48169	0.48191	−22

STRUCTURE DETERMINATION

The intensity distribution indicated the crystal class to be $6mm$ or $6/mmm$. Systematic absences of $hh\bar{l}$ 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 Å^3), Au_3Hg (17.5 Å^3), and Hg (23.4 Å^3) to a composition $Au_{.54}Hg_{.46}$ gives a mean atomic volume of about 18.3 Å^3, and a content of 22 atoms within one unit cell. The observed density was 16.3 g cm^{-3} and a calculated density for $Au_{12}Hg_{10}$ 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,*z* 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 $P6_3cm$ 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 gold [1] (2.88—2.90 Å) and in mercury metal (3.005 and 3.470 Å) showed that a centrosymmetrical 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 Au_6Hg_5. $R=7.6$ %.

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 0 4	47	74	0 1 8	5	7	3 1 8	74	79	3 2 3	332	325
0 0 6	361	454	1 1 0	148	138	3 1 9	160	164	3 2 4	196	184
0 0 8	630	842	1 1 1	73	66	4 1 0	400	379	3 2 5	126	120
0 0 10	287	302	1 1 2	363	375	4 1 1	52	45	3 2 6	114	114
1 0 0	84	72	1 1 3	542	647	4 1 2	271	271	3 2 7	268	256
1 0 2	30	18	1 1 4	296	280	4 1 3	96	91	3 2 8	63	63
1 0 4	491	460	1 1 5	367	334	4 1 4	77	80	4 2 0	353	337
1 0 6	167	156	1 1 6	439	424	4 1 5	76	67	4 2 1	99	105
1 0 10	132	115	1 1 7	202	176	4 1 6	81	82	4 2 2	10	23
2 0 0	160	138	1 1 8	70	47	4 1 7	31	26	4 2 3	201	204
2 0 2	434	416	1 1 9	185	172	5 1 0	254	257	4 2 4	33	19
2 0 4	340	316	1 1 10	110	126	5 1 1	115	105	4 2 5	160	154
2 0 6	198	183	2 1 0	390	428	5 1 2	31	24	4 2 6	98	82
2 0 8	55	45	2 1 1	437	484	5 1 3	282	288	5 2 0	142	137
2 0 10	325	327	2 1 2	136	127	5 1 4	52	53	5 2 1	163	177
3 0 0	524	517	2 1 3	257	262	5 1 5	120	131	5 2 2	41	41
3 0 2	148	128	2 1 4	86	78	6 1 0	293	319	5 2 3	270	260
3 0 4	201	188	2 1 5	12	8	2 2 0	55	35	0 3 6	8	12
3 0 8	325	325	2 1 6	59	51	2 2 1	164	160	3 3 0	132	123
4 0 0	476	486	2 1 7	500	489	2 2 2	154	131	3 3 1	405	406
4 0 2	50	26	2 1 8	255	239	2 2 3	20	19	3 3 2	215	197
4 0 4	625	610	2 1 9	93	79	2 2 4	403	415	3 3 3	195	179
4 0 6	348	339	2 1 10	175	173	2 2 5	40	62	3 3 4	279	275
4 0 8	255	235	3 1 0	74	64	2 2 6	246	239	3 3 5	11	33
5 0 0	421	426	3 1 1	229	216	2 2 7	144	146	3 3 6	307	305
5 0 2	282	274	3 1 2	78	72	2 2 8	58	65	4 3 0	24	16
5 0 4	100	86	3 1 3	290	273	2 2 9	73	61	4 3 1	90	83
5 0 6	391	401	3 1 4	395	383	3 2 0	136	131	4 3 2	89	80
6 0 0	67	62	3 1 5	248	225	3 2 1	206	197	4 3 3	28	21
6 0 2	216	193	3 1 6	58	52	3 2 2	280	258	4 3 4	103	109
6 0 4	170	190	3 1 7	157	151						

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.

Atom—Atom	CN	Dist.	S.D.
Au —Au	2	2.797	0.006 Å
—Au	1	2.799	0.005 Å
—Au	1	2.844	0.007 Å
—Hg(1)	2	2.890	0.004 Å
—Au	2	2.926	0.005 Å
—Hg(2)	2	2.930	0.002 Å
Hg(1)—Au	2	2.799	0.005 Å
—Au	4	2.890	0.004 Å
—Hg(2)	4	3.298	Å
Hg(2)—Au	6	2.930	0.002 Å
—Hg(1)	6	3.298	Å

Final positional and thermal parameters were:

12(k) Au	$x = 0.2416 \pm 5$,	$y = 0$,	$z = 0.3902 \pm 4$,	$B = 0.52 \pm 9$ Å^2
6(g) Hg(1)	$x = 0.5864 \pm 7$,	$y = 0$,	$z = 1/4$,	$B = 0.63 \pm 11$ Å^2
4(d) Hg(2)	$x = 1/3$,	$y = 2/3$,	$z = 0$,	$B = 0.62 \pm 12$ 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

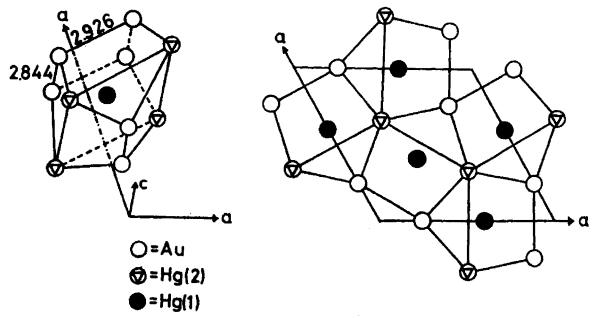

Fig. 1. The 10-coordination polyhedron around Hg(1) and one layer of polyhedra projected along the c-axis.

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 Hg(2)—Hg(2) edges with the lower layer.

The 12-coordination around 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 Hg(1) above and three below at a distance of 3.298 Å and an irregular staggered 6-membered ring of gold at a distance of 2.930 Å. In mercury metal the corresponding distances are 2.999 Å and 3.463 Å.

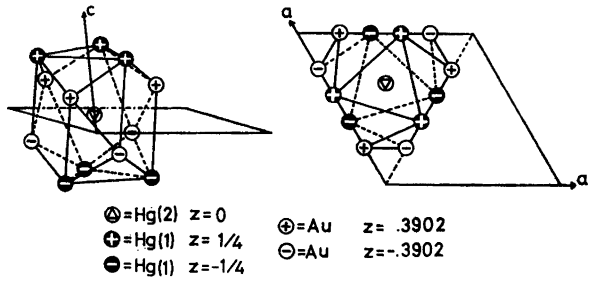

Fig. 2. The 12-coordination polyhedron around Hg(2) and its projection in the *c*-direction.

The structure may also be described with the 12-coordination polyhedron around 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 Au—Hg(1)—Au—Hg(1) parallelograms and one on each side along the three-fold axis sharing the regular Hg(1)—Hg(1)—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 Å.

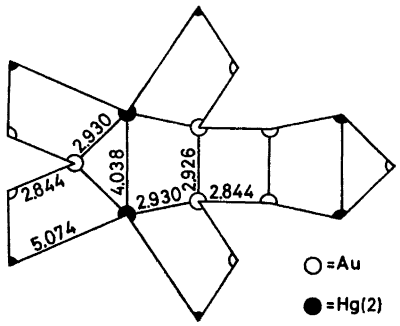

Fig. 3. Template for construction of the 10-coordination polyhedron around Hg(1).

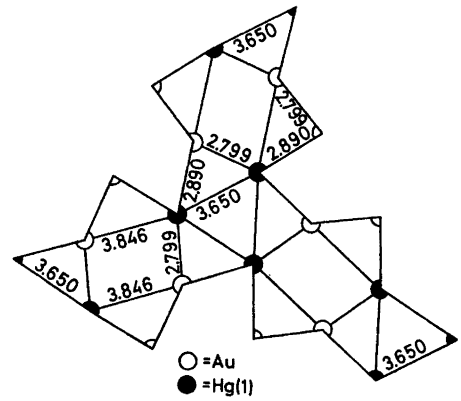

Fig. 4. Template for construction of the 12-coordination polyhedron around Hg(2).

Crystals of Au_6Hg_5 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, Au_3Hg, or Au_6Hg_5, 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

1. Pabst, A. *Z. physik. Chem.* **B 3** (1929) 443.
2. Stenbeck, S. *Z. anorg. allgem. Chem.* **214** (1933) 16.
3. Plaksin, I. N. *Izv. Sekt. Fiz. Khim. Anal., Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR* **10** (1938) 129.
4. Winterhager, H. and Schlosser, W. *Metall* **14** (1960) 1.
5. Kulifay, S. M. *J. Am. Chem. Soc.* **83** (1961) 4916.
6. Cromer, D. T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.
7. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
8. *IUCr Word List of Crystallographic Computer Programs*, 2nd Ed., Cambridge, Mass. 1966.

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