The Crystal Structure of the Au₂Hg Phase

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The compound in the Au–Hg system richest in Hg has been reported to be Au₂Hg. The crystal structure of this compound has been determined by single-crystal X-ray methods and has been found to be a new structure type. The unit cell is hexagonal with $a = 7.019$, $c = 10.184$ Å and contains 22 atoms. The space group is $P6_3/mcm$ and the calculated density is 16·67 g.cm⁻³. The structure was refined by least-squares methods to a conventional R index of 0·127, using multiple-film, equi-inclination Weissenberg data. The structure is disordered. Au and Hg atoms could not be distinguished because of the similarity of their scattering factors. The average nearest-neighbor distance is 2·89 Å. The structure is loosely packed with 12 of the atoms in the unit cell having 10 nearest neighbors and the other 10 having only six.

Introduction

The literature relating to the Au–Hg phase diagram and the compounds which exist in this system contains conflicting reports. The phase diagram presented by Hansen (Hansen & Anderko, 1958) suggests the existence of Au₃Hg and AuHg₂ (or Au₂Hg₃). A third phase with stoichiometry close to Au₂Hg or AuHg is also indicated. Numerous other compounds of various stoichiometries have been proposed by several authors (Braley & Schneider, 1921; Pabst, 1929; Stenbeck, 1933). Winterhager & Schlosser (1960) reported that the compounds Au₃Hg, Au₂Hg₃ and AuHg₂ appeared to be present.

A recent redetermination of the complete phase diagram of the Au–Hg system (Rolfe & Hume-Rothery, 1967) has resolved much of the confusion. They report the existence of only three compounds: Au₃Hg, a compound somewhat richer in Au than Au₃Hg, and a compound near the composition Au₂Hg. Au₃Hg is known to have the $A3$ structure (Stenbeck, 1933; Massalski, 1957). The powder data for Au₂Hg presented by Rolfe & Hume-Rothery (1967) do not agree with those given by Pabst (1929) nor with those of Winterhager & Schlosser (1960). In order to increase our understanding of the Au–Hg system, a determination of the structure of the Au₂Hg phase was undertaken.

Preparation of samples

Compounds were prepared by the co-reduction method of Kulifay (1961). Stoichiometric amounts of HAuCl₄.2H₂O and HgO were dissolved in $3M$ HNO₃, to give approximately $0.1M$ solutions. These were added slowly to a boiling mixture of ten parts by volume

of $4M$ NH₄OH and one part of 85% N₂H₄.H₂O. All chemicals used were Fischer reagent grade. The amalgams resulting from this co-reduction were placed under vacuum and heated to 110°C for 2 hours to remove any excess Hg.

Samples were prepared for various stoichiometries richer in Hg than Au₂Hg, and X-ray powder patterns were taken before and after heating. All powder patterns obtained were identical with each other and with the powder pattern reported by Rolfe & Hume-Rothery (1967) for Au₂Hg.

X-ray data

The samples contained numerous, small, needle-like crystals. The crystal chosen for data collection was approximately 0·04 mm in diameter and 0·5 mm in length and was mounted with the long dimension coincident with the axis of rotation. Multiple-film, equi-inclination Weissenberg data were collected for the reciprocal levels $hk0$ through $hk5$ with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). The intensities were estimated visually using a calibrated intensity strip and were corrected for Lorentz and polarization effects.

An absorption correction was applied, assuming a cylindrical crystal of average radius 0·02 mm, and using the transmission factors of Bradley (1935) for Cu $K\alpha$ radiation ($\mu R = 8$ for the $hk0$ reciprocal layer). A separate scale factor was used for each reciprocal level in the final three-dimensional refinement to minimize errors due to absorption.

Unit cell and space group

The c lattice-constant was determined from a rotation photograph calibrated by superposition of a sodium chloride diffraction pattern ($a = 5.6402$ Å). The lattice constant a was determined by measurement of the $h00$ spot positions on an uncalibrated $hk0$ Weissenberg

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photograph. Standard deviations in the lattice constants were estimated by least-squares analyses.

The unit cell is hexagonal with $a = 7\cdot019 \pm 0\cdot017$, $c = 10\cdot184 \pm 0\cdot025$ Å. The Laue symmetry is $6/mmm$. Systematic absences of $h0l$ reflections for l odd indicate the space group to be $P6_3/mcm$, $P6_3cm$, or $P\bar{6}c2$. Of these only $P6_3/mcm$ is centrosymmetric and this space group was confirmed by solution of the structure.

Structure determination

The initial stages of the structure determination were carried out using $hk0$ data. An (001) Patterson projection* was used along with packing arguments to provide a trial structure. If the compound has stoichiometry Au_2Hg and if the density of packing is comparable to that in Au_3Hg then there should be 24 atoms in the unit cell. These were placed in the following positions of $P6_3/mcm$: 12 atoms in $12(k)$, $\pm(x_1, 0, z_1; 0, x_1, z_1; \bar{x}_1, \bar{x}_1, z_1; x_1, 0, \frac{1}{2}-z_1; 0, x_1, \frac{1}{2}-z_1; \bar{x}_1, \bar{x}_1, \frac{1}{2}-z_1)$; 6 atoms in $6(g)$, $\pm(x_2, 0, \frac{1}{4}; 0, x_2, \frac{1}{4}; \bar{x}_2, \bar{x}_2, \frac{1}{4})$; 4 atoms in $4(c)$, $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4}; \frac{2}{3}, \frac{1}{3}, \frac{1}{4})$; or $4(d)$, $\pm(\frac{1}{3}, \frac{2}{3}, 0; \frac{1}{3}, \frac{2}{3}, \frac{1}{2})$; 2 atoms in $2(b)$, $(0,0,0; 0,0,\frac{1}{2})$; or $2(a)$, $\pm(0, 0, \frac{1}{4})$. The fourfold and twofold sets of positions are identical in projection. The approximate parameters were $x_1 \simeq 0\cdot25$ and $x_2 \simeq 0\cdot6$. Since the scattering factors of Au and Hg are nearly identical no attempt was made to distinguish between the two types of atom.

The trial structure was refined by least-squares calculations to an unweighted discrepancy index, $R = (\sum |F_o - F_c| / \sum |F_o|)$, of $0\cdot24$. The function minimized was $\sum \omega(F_o - F_c)^2$ with weights assigned according to: $\sqrt{\omega} = 1/F_o$ for $F_o \geq 4F_{min}$; $\sqrt{\omega} = 1/4F_{min}$ for $F_o \leq 4F_{min}$. The scattering factors for Au and Hg were taken from International Tables for X-ray Crystallography (1962).

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* All computations described in this paper were performed on the IBM 1130 8K computer available at the University of Missouri–St. Louis, using ad hoc programs written by one of the authors (A.F.B.).

The large value of R at this stage of the refinement, for projection data, was unacceptable. A difference electron density projection onto (001) showed a large negative peak at the origin. Continued refinement after exclusion of the atoms in a twofold position gave $R = 0\cdot07$.

A chemical analysis by the electrodeposition technique described by Lingane (1966), of the sample from which the crystal for data collection was taken, showed $37\cdot0 \pm 0\cdot3\%$ Hg. This value is consistent with that calculated for the ideal composition Au_7Hg_4 ($36\cdot79\%$ Hg), corresponding to 22 atoms in the unit cell. However, since the stoichiometry Au_7Hg_4 or Au_2Hg cannot be satisfied by distribution of atoms among a twelve-fold, sixfold, and fourfold position, it must be concluded that this compound contains substitutional disorder.

The density calculated for 14 Au and 8 Hg atoms in the unit cell is $16\cdot67$ g.cm^{-3}. The experimental density could not be obtained because of the small amount of sample.

The value of z_1 was estimated from packing arguments to be about $0\cdot1$ and the structure was refined by least-squares, using all the data, to a final R of $0\cdot127$. A separate scale factor for each reciprocal layer and a single, isotropic temperature factor were included in the calculation as refinable parameters. No correc-

Table 1. *Atomic positions and final parameters*

Atom type	Position	Final parameters
1	$12(k)$	$x_1 = 0\cdot2435$ (1)
		$z_1 = 0\cdot1150$ (3)
2	$6(g)$	$x_2 = 0\cdot5878$ (2)
3	$4(d)$	

Temperature factor $B = 3\cdot2$ (1) Å

Table 2. *Observed and calculated structure factors*

A minus sign in the F_{obs} column means 'less than'.

h k l	F_{obs}	F_{calc}		h k l	F_{obs}	F_{calc}		h k l	F_{obs}	F_{calc}
1 0 0	83	68		1 0 2	-198	-1		1 3 4	544	-423
2 0 0	156	-138		2 0 2	420	373		2 0 4	342	279
3 0 0	468	478		3 0 2	103	98		3 0 4	171	143
4 0 0	371	375		4 0 2	-77	5		4 0 4	404	-452
5 0 0	256	274		5 0 2	173	-197		5 0 4	-88	-45
6 0 0	-52	-33		6 0 2	111	112		6 0 4	-80	103
7 0 0	-59	72		7 0 2	86	-96		7 0 4	-52	-38
1 1 0	122	-145		1 1 2	433	374		1 1 4	331	259
2 1 0	351	-385		2 1 2	85	-100		2 1 4	-100	70
3 1 0	-58	-49		3 1 2	-77	59		3 1 4	242	-295
4 1 0	286	263		4 1 2	201	180		4 1 4	-93	-53
5 1 0	162	-166		5 1 2	-70	-16		5 1 4	-85	-22
6 1 0	163	-157		6 1 2	-63	-8		6 1 4	-77	-7
7 1 0	83	71		7 1 2	55	58		7 1 4	-50	7
2 2 0	-58	22		2 2 2	129	125		2 2 4	291	316
3 2 0	93	-98		3 2 2	201	-183		3 2 4	-96	134
4 2 0	222	-220		4 2 2	-72	-6		4 2 4	-86	-14
5 2 0	81	77		5 2 2	-63	-16		5 2 4	256	206
6 2 0	111	-105		6 2 2	-40	-14		6 2 4	-50	4
3 3 0	76	-69		3 3 2	141	133		3 3 4	-88	165
4 3 0	-48	10		4 3 2	-63	-45		4 3 4	-77	-65
5 3 0	49	53		5 3 2	-46	-44		5 3 4	-55	-53
4 4 0	248	193		4 4 2	126	123		4 4 4	179	-130
1 1 1	-90	-67		1 1 3	616	-582		1 1 5	414	335
2 1 1	405	-447		2 1 3	219	-200		2 1 5	-99	34
3 1 1	141	182		3 1 3	178	-204		3 1 5	182	160
4 1 1	-65	-26		4 1 3	72	53		4 1 5	-93	-40
5 1 1	-60	-80		5 1 3	172	-161		5 1 5	-86	78
6 1 1	55	-54		6 1 3	257	-159		6 1 5	78	91
7 1 1	54	-36		7 1 3	-45	8		2 2 5	-93	-48
2 2 1	137	-176		2 2 3	80	36		3 2 5	-92	-91
3 2 1	140	158		3 2 3	201	218		4 2 5	-86	-85
4 2 1	81	-77		4 2 3	78	117		5 2 5	-76	58
5 2 1	105	-98		5 2 3	141	-124		3 3 5	-86	-5
6 2 1	79	-68		6 2 3	-45	12		4 3 5	-75	21
3 3 1	265	201		3 3 3	95	93		4 4 5	54	-60
4 3 1	-54	52		4 3 3	-70	-20				
5 3 1	-38	-3		5 3 3	-50	-25				
4 4 1	93	-77		4 4 3	-50	60				

Fig. 1. Projection of the structure onto the (001) plane. The numbers in the circles are the z coordinates. For each atom at z there is another, equivalent atom at $\frac{1}{2} - z$.

tions were applied for anomalous dispersion or extinction. Unobserved reflections were not included. The final atomic parameters and the temperature factor are given in Table 1. The numbers in parentheses are the standard deviations in the least significant figure as estimated from the least-squares analysis.

Table 2 lists the observed and calculated structure factors scaled to $F(000)$. The total number of electrons per unit cell, $F(000)$, is 1906.

Discussion

The unit cell contains 22 atoms in three sets of equivalent positions. There are 12 atoms of type 1 in 12(k), 6 of type 2 in 6(g), and 4 of type 3 in 4(d). Interatomic distances are listed in Table 3. A projection of the structure onto the (001) plane is illustrated in Fig. 1.

Table 3. Interatomic distances

Reference atom	Coordinated atom	Number of coordinated atoms	Distance
1	1	1	2·750 (9) Å
	1	2	2·900 (9)
	1	2	2·960 (7)
	2	1	2·780 (8)
	2	2	2·870 (8)
	3	2	2·953 (8)
2	1	2	2·780 (8)
	1	4	2·870 (8)
	3	4	3·312 (8)
3	1	6	2·953 (8)
	2	6	3·312 (8)

The coordination polyhedra about the three types of atoms are shown in Fig. 2. In each drawing the [001] axis is vertical and the (1$\bar{1}$0) plane is parallel to the paper. The size of each circle is inversely proportional to the distance from the observer. The number in each circle refers to the atom type and the central atom is unlabelled.

Each atom of type 1 and type 2 is surrounded by a distorted pentagonal prism [Fig. 2(a) and (b)]. The coordination shell around each atom of type 3 may be described as a distorted hexagonal prism [Fig. 2(c)], the two hexagons of which are considerably puckered.

The nearest-neighbor distance averaged over all bonds in the unit cell is 2·888 Å. For comparison, the average interatomic distance in Au₃Hg is 2·925 Å (Stenbeck, 1933). If only nearest neighbors are considered then atoms of types 2 and 3 have sixfold coordination. The average coordination number is therefore 8·2. The weighted sum of the Pauling radii (Pauling, 1947) for coordination number 8·2 is 2·897 Å in pleasing agreement with the experimental value of 2·888 Å.

If a hard sphere model is assumed with each atom having a diameter of 2·888 Å then the density of packing as measured by the ratio of the total volume of the

(a)

(b)

(c)
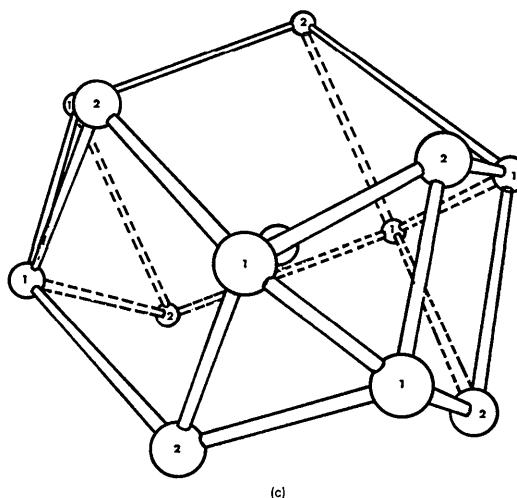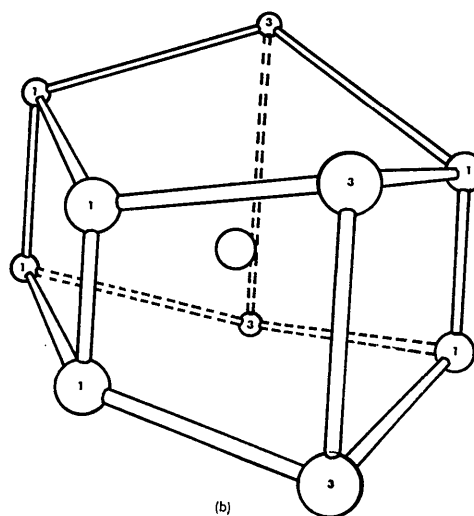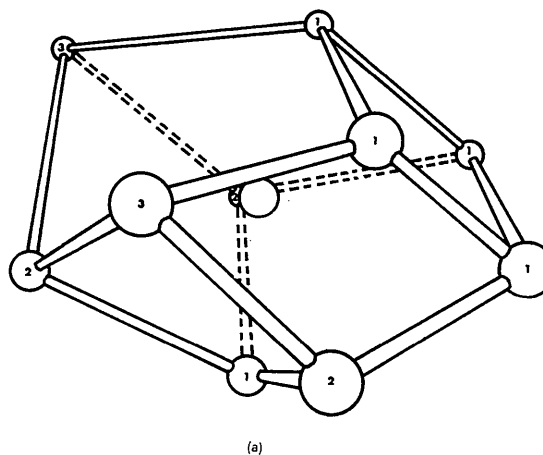
Fig. 2. Coordination polyhedra about (a) atoms of type 1, (b) atoms of type 2, (c) atoms of type 3.

atoms divided by the volume of the unit cell is 0·64. This structure is less densely packed than a b.c.c. structure for which this ratio is 0·68, but is more densely packed than crystalline Hg (at 227°K) for which this ratio is 0·61.

The low density of packing, the low coordination numbers, and the existence of short interatomic distances at 2·750 and 2·780 Å suggest that the bonding is not entirely metallic in nature but has some covalent character.

Conclusions

Rolfe & Hume-Rothery (1967) have presented powder data for a compound they identify as Au_2Hg. Powder patterns prepared from our samples and the single-crystal data are all in excellent agreement with their data. This proves the identity between the compound they call Au_2Hg and the compound described here. Since the structure is disordered the exact stoichiometry could not be determined. The structure of the Au_2Hg phase is a new structure type.

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Barium Aluminate Hydrates. II. The Crystal Structure of Ba2[Al2(OH)10]

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The compound $2BaO.Al_2O_3.5H_2O$ has been shown by X-ray structural analysis to contain complex anions of formula $[Al_2(OH)_{10}]^{4-}$, which are built from two $Al(OH)_6$ octahedra sharing an edge. These are linked by the barium ions and by hydrogen bonding. The compound is thus a complex hydroxide and the formula should be written $Ba_2[Al_2(OH)_{10}]$.

Introduction

The compound of empirical formula $2BaO.Al_2O_3.5H_2O$ has been known for some time, having first been prepared by Beckmann (1882) who boiled together unspecified quantities of hydrated alumina and baryta water, and concentrated the filtrate by boiling. Morphological data for his product, which was triclinic, are given in Table 1. Many subsequent preparations have been reported and its stability relationships have been investigated (*e.g.* Malquori, 1926; Carlson & Wells, 1948; Carlson, Chaconas & Wells, 1950).

Table 1. *Crystal data for* $Ba_2[Al_2(OH)_{10}]$

Unit cell

$a = 6·70_4$	$b = 5·75_8$	$c = 6·17_9$ Å
$\alpha = 90°4'$	$\beta = 98°25'$	$\gamma = 109°36'$
$P\bar{1}$	$Z = 1$	X-ray density 3·723 g.cm^{-3}

Table 1 (*cont.*)

Goniometric data

(1) $a:b:c$ 0·8545:1:0·9888	(2) $a:b:c$ 0·859:1:0·922
$\alpha = 99°20\frac{1}{2}'$	$\alpha = 98°25'$
$\beta = 91°52'$	$\beta = 90°4'$
$\gamma = 109°26\frac{1}{2}'$	$\gamma = 109°36'$

Refractive indices and observed density

	Carlson & Wells (1948)	Present work
α	1·642	1·643 ± 0·003
β	1·655	1·655 ± 0·003
γ	1·676	1·675 ± 0·003
D_{obs}	3·42 g.cm^{-3}	3·66 g.cm^{-3}

(1) Quoted by Beckmann (1882).
(2) Calculated from the X-ray cell transformed into Beckmann's setting.

In the present work it was found possible to prepare the compound by many methods. Beckmann's original