82. *The Crystal Structure of Tribromo(trimethylphosphine)gold.*

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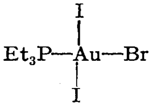
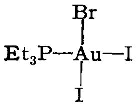
The crystal structure of PMe_3–$AuBr_3$ was determined by the usual methods of *X*-ray analysis. The crystals are orthorhombic, with eight molecules in the unit cell, and belong to the space-group *Pbca*. Trial-and-error as well as Fourier methods were employed in order to determine the positions of the molecules. The parameters finally assigned to the gold and bromine atoms were checked by comparison between observed and calculated structure amplitudes of the *h0l*, *0kl* and *3kl* reflections which were found to be in good agreement. The position of the phosphine groups had to be inferred from considerations of optimum packing. The crystal structure is of the layer type, with molecules in neighbouring layers pointing in opposite directions. The co-ordination around the auric gold atoms is planar, in conformity with the findings of previous investigators, and the gold–bromine distance is 2·5 A.

THIS structure analysis was begun at the suggestion of Dr. F. G. Mann, who had observed that certain derivatives of four-covalent auric gold failed to show the geometric isomerism which their (probable) planar structure and their method of preparation would lead one to expect (Mann and Purdie, *J.*, 1940, 1235). Compounds of 2-covalent aurous gold were known to have a linear structure (*e.g.*, $AsEt_3$–$AuCl$; Mann, Wells, and Purdie, *J.*, 1937, 1835), whereas derivatives of 4-covalent auric gold have a planar structure (Buraway, Gibson, Hampson, and Powell, *J.*, 1937, 1690; Phillips and Powell, *Proc. Roy. Soc.*, 1939, *A*, **173**, 147; see also Elliot and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 1946). The compound PEt_3–$AuBrI_2$, should therefore exist in the form of two geometric isomers, (I) and (II), depending on whether it is prepared by the addition of iodine to PEt_3–$AuBr$ or of iodine monobromide to PEt_3–AuI. When Mann and Purdie failed to obtain the expected

(I.) 

$$Et_3P\text{—}\underset{\displaystyle I}{\overset{\displaystyle I}{Au}}\text{—}Br$$

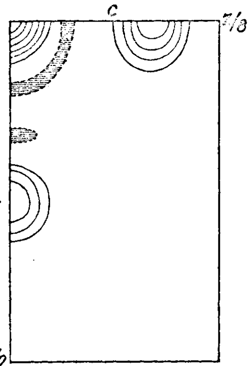
 (II.)

$$Et_3P\text{—}\underset{\displaystyle I}{\overset{\displaystyle Br}{Au}}\text{—}I$$

cis- and *trans*-forms, either of this compound or of three other related ones, they were forced to conclude either that the co-ordination around the gold atom is tetrahedral, or more probably, that the groups around the gold atom have a certain mobility and tend to take up the most stable configuration, no matter how the compound is prepared.

The calculation of a single Fourier projection of PMe_3–$AuBr_3$ sufficed to show that the co-ordination around the gold atom is, in fact, planar, and that Mann and Purdie's second suggestion must therefore account for the absence of stereoisomerism in trihalide compounds containing different halogen atoms. Although the point at issue was thus settled without any need to resort to a complete structure analysis, it was nevertheless decided to carry our investigation one stage further and to establish the main interatomic distances and general manner of packing of the molecules in the crystal. Fourier syntheses as well as trial-and-error methods were used to work out the parameters of gold and bromine; the positions of the carbon and phosphorus atoms, on the other hand, had to be inferred from considerations of packing, because their relative scattering contribution was too feeble to have a measurable influence on the intensities of any of the observed reflections.

FIG. 1.



Relative electron-density projection on (010), *showing one-sixteenth of the unit cell. Contours of equal electron density are drawn at arbitrary intervals, every alternate contour on the gold atom being omitted; the lowest contour is shown as a dashed line. The shaded areas indicate electron-density troughs due to the diffraction effects of the two superimposed gold atoms.*

Details of Analysis.—Dr. Mann kindly supplied the crystals, which are lath-shaped, orthorhombic, yellow needles showing straight extinction on all faces and marked dichroism in two planes. The vibration direction of greatest light absorption is parallel to [100] and coincides with the vibration direction of the slowest ray, indicating that the molecules in the crystal lattice are arranged with their length along the *a* axis. This was subsequently confirmed by *X*-ray analysis. The unit cell-dimensions were determined by oscillation photographs taken about the three axes; they are $a = 9{\cdot}0_6$, $b = 9{\cdot}8_5$, $c = 22{\cdot}0_5$ A. The density of the crystals as determined by pyknometer methods is 3·37 g./c.c., giving eight molecules per unit cell. A pseudo-cell containing only two molecules is indicated, however, by the extreme weakness of the odd layer lines on photographs taken with *b* and *c* as rotation axes.

The oscillation photographs showed that there are no absences of the general type *hkl*. The special absences *0kl* for *k* odd, *h0l* for *l* odd, and *hk0* for *h* odd were found and later confirmed on Weissenberg photographs taken about the three axes; these gave the space-group unambiguously as *Pbca*. In addition to the space group absences, *h0l* reflections were found to be missing for $h + \frac{l}{2} = 2n + 1$, a feature of the *X*-ray pattern which greatly simplified the analysis and actually provided the clue to the disposition of the molecules on the *b* projection.

There was, in fact, only one set of molecular positions which would account for the absence of those reflections : the molecules had to be placed with their length along the *a* axis, in the positions $z = 1/8$, $z = 3/8$, etc. It can be seen in Fig. 2 that this brings the molecules to the corners and the centre of the " halved " *b* face—the two halves from $z = 0$ to $z = \frac{1}{2}$ and from $z = \frac{1}{2}$ to $z = 1$ appearing identical in projection. Moreover, a one-dimensional Patterson projection on [100] indicated that the gold atoms lie at $x = \frac{1}{4}$ and $x = \frac{3}{4}$, thus leaving only four positions for the eight gold atoms in the unit cell; the gold atoms of pairs of molecules related by the *b* glide planes therefore come to be superimposed, with the result that the relative scattering contribution of these " doubled " gold atoms outweighs the combined contributions of all the other atoms in the unit cell and thus determines the phases of all *h*0*l* reflections. A Fourier projection on the *x*, *z* plane could therefore be calculated without having to make any further assumptions about the structure (Fig. 1).

Visually estimated relative intensities obtained from Weissenberg photographs were used to determine the values of F'_{h0l}; the result of the Fourier summation shows, of course, the gold and bromine atoms but not the phosphine groups. A foreshortening of one of the gold–bromine distances indicates that the plane of the molecule is inclined to the plane of the projection. The *x* and *z* co-ordinates of the gold and bromine atoms derived from this Fourier projection were confirmed by comparison of calculated and observed F's, which agreed satisfactorily (Table I*a*). In these calculations it was assumed that the phosphorus peak is

TABLE I.

Comparison of observed and calculated structure amplitudes, arranged in order of decreasing values of θ.

$$F' \text{ calc.} = \frac{1}{10} F e^{-2\sin^2\theta/\lambda^2}, \quad F' \text{ obs.} = k\sqrt{I_B \frac{1 + \cos^2 2\theta}{\sin 2\theta}},$$

where I_B represents the visually estimated relative intensity of the reflection on the Weissenberg photograph and k is an arbitrary factor determined from the equation

$$k_{h0l} = \Sigma F' \text{ calc.}/\Sigma\sqrt{I_B \frac{1 + \cos^2 2\theta}{\sin 2\theta}}.$$

The quality of the agreement in each case is shown by the expression

$$\Sigma\Delta F'_{h0l}/\Sigma F'_{h0l}, \text{ calc.}$$

where $\Delta F'$ is the numerical difference between F′ calc. and F′ obs. No corrections for absorption or extinction were applied.

TABLE I*a*.

$k_{h0l} = 13{\cdot}5$; $\Sigma\Delta F'_{h0l}/\Sigma F'_{h0l}$, calc. $= 0{\cdot}20$.

Absences of the type $F'_{h0l} = 0$ for $h + \frac{l}{2} = 2n + 1$ are omitted.

Index.	F′, calc.	F′, obs.	Index.	F′, calc.	F′, obs.	Index.	F′, calc.	F′, obs.	Index.	F′, calc.	F′, obs.
102	− 77	53	502	−38	40	2,0,16	+ 3	0	5,0,18	− 2	0
004	− 64	57	3,0,10	−70	66	702	−53	47	7,0,14	+33	27
200	+ 72	59	408	+46	54	706	+19	28	902	−16	19
204	− 2	0	2,0,12	−47	53	5,0,14	+20	28	1,0,22	+32	43
106	+ 3	0	506	+ 6	0	4,0,16	+22	30	4,0,20	−28	30
302	− 85	86	1,0,14	+38	51	6,0,12	−39	32	8,0,12	−36	26
008	+ 65	55	600	+51	43	3,0,18	−14	19	3,0,22	+36	36
306	+ 22	20	604	− 9	0	800	+47	42	0,0,24	+39	35
208	+ 10	0	4,0,12	−72	72	7,0,10	−47	36	2,0,24	+20	31
400	+104	108	3,0,14	+45	49	804	−17	27	6,0,20	−11	0
1,0,10	− 64	74	5,0,10	−21	38	0,0,20	−35	35	5,0,22	+21	23
404	+ 43	61	0,0,16	+29	35	2,0,20	−10	0	8,0,16	+ 9	18
0,0,12	− 92	104	608	+14	0	808	+20	30	4,0,24	+33	31
						6,0,16	+ 3	0			

TABLE I*b*.

$k_{0kl} = 33{\cdot}3$, except for $k_{0k0} = 14{\cdot}2$; $\Sigma\Delta F'_{0kl}/\Sigma F'_{0kl}$, calc. $= 0{\cdot}26$.

Absences of the type $F'_{0kl} = 0$ for $l = 2(2n + 1)$ are omitted.

Index.	F′, calc.	F′, obs.	Index.	F′, calc.	F′, obs.	Index.	F′, calc.	F′, obs.	Index.	F′, calc.	F′, obs.
004	−64	53	061	+27	27	0,4,15	−19	0	0,4,20	−30	36
021	−11	13	0,2,13	+10	0	0,2,17	0	0	0,8,13	+18	10
023	+37	33	049	+ 6	0	0,6,12	+50	57	0,10,1	+ .7	0
024	+71	73	063	+14	0	081	− 4	0	0,10,3	+ 9	10
025	− 0	13	064	+31	53	083	−24	20	0,10,5	−18	20
008	+65	70	0,4,11	−11	10	0,4,16	+45	57	0,8,15	+ 5	0
027	+ 5	13	065	− 4	0	084	−32	53	0,10,7	−17	17
041	−20	17	0,4,12	−35	37	085	+16	0	0,10,9	+ 6	7
028	−78	80	067	− 5	0	0,6,13	−17	17	0,8,16	+22	27
043	+ 7	0	068	−34	53	087	+13	0	0,0,24	+39	40
044	−74	77	0,2,15	−20	20	088	+27	47	0,2,24	−21	20
029	+28	23	0,4,13	+18	0	0,0,20	−35	40			
045	+26	23	0,0,16	+29	50	0,6,15	− 6	0	020	−66	55
047	+29	20	069	+ 3	0	0,2,20	+35	47	040	+49	45
0,2,11	+ 2	0	0,2,16	−55	63	0,8,11	− 7	0	060	−72	77
0,0,12	−94	100	0,6,11	+22	17	0,6,16	−18	30	080	+23	38
0,2,12	+44	63				0,8,12	−18	33	0,10,0	−18	30

TABLE I*c*.

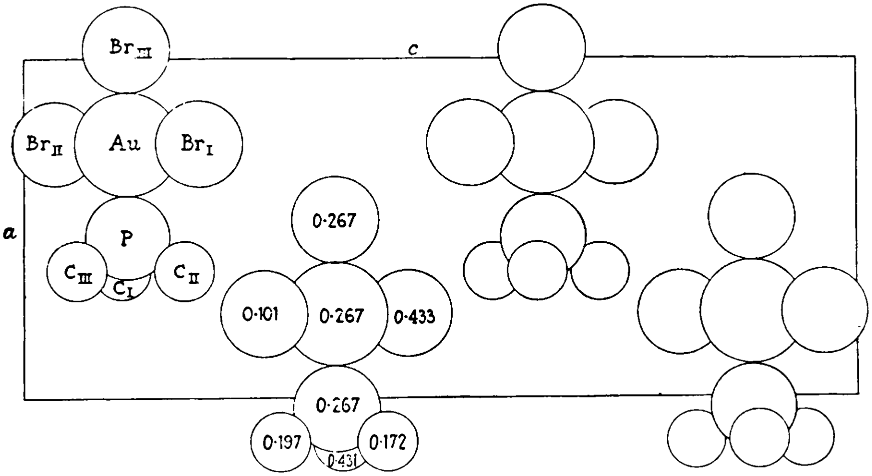
$k_{3kl} = 11{\cdot}0$; $\Sigma\Delta F'_{3kl}/\Sigma F'_{3kl}$, calc. $= 0{\cdot}26$.

Absences of the type $F'_{3kl} = 0$ for $l = 4n$ are omitted.

Index.	F′, calc.	F′, obs.	Index.	F′, calc.	F′, obs.	Index.	F′, calc.	F′, obs.	Index.	F′, calc.	F′, obs.
302	−84	137	326	−72	78	347	− 1	0	3,4,14	+29	24
311	+ 1	13	327	+10	18	349	+ 6	19	3,6,10	+38	29
312	+23	18	341	+ 5	0	3,4,10	−31	30	3,0,18	−14	0
313	− 2	0	319	+12	14	361	+19	15	381	− 8	0
321	+17	18	342	−40	37	362	+41	47	382	−18	28
322	+52	50	343	− 9	24	363	−11	18	383	+15	0
323	−27	25	3,0,10	−70	75	3,0,14	+45	53	3,2,18	+37	28
315	− 2	9	329	+22	22	365	− 1	0	386	+25	24
306	+22	27	3,1,10	+ 7	0	3,2,14	−35	31	3,6,14	−26	22
325	−16	16	345	+ 6	0	366	−12	22	3,4,18	−32	22
316	−12	13	346	+57	63	367	+ 1	0	3,8,10	−14	21
317	+ 2	0	3,2,10	+36	41						

superimposed on one of the bromine peaks, and that the gold–phosphorus distance is 2·5 A., the sum of the atomic radii. Fig. 2 is drawn on the basis of the Fourier projection, as far as the gold and bromine atoms are concerned, and shows the arrangement of the molecules.

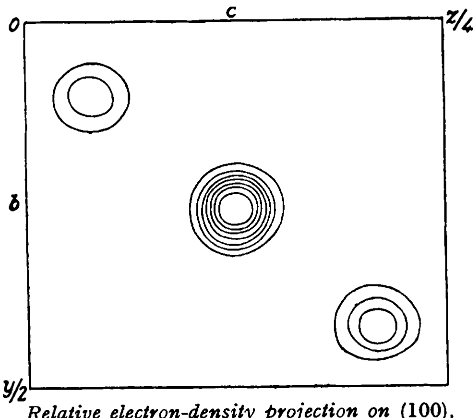
FIG. 2.



Unit cell projected on (010). *The meaning of the different circles is indicated on the molecule in the left-hand top corner. For the sake of clarity only one of the two layers of molecules in the unit cell is shown. The molecules in the second layer would show* Au, Br_I, *and* Br_{II} *in identical positions, while the positions of* Br_{III} *and the phosphine groups would be interchanged. The figures indicate* y *co-ordinates.* (1 *cm.* = 2 A.)

It now remained to find the *y* parameters of the gold and bromine atoms, and the *a* projection was chosen as the most suitable for this purpose. The relative intensities of the 0*kl* reflections, again read from Weissenberg photographs, were first used to calculate a Patterson projection from which the gold–bromine vector could at once be derived; its length was 2·5 A. and it enclosed an angle of 41° with the *c*-axis. Having thus determined the only intramolecular vector which appears on the *a* projection, we found the *y* parameter of the gold atom in the following way. It has been mentioned above that the weakness of reflections with odd *l* indices indicated the existence of a pseudo-cell with only half the length of *c*. In this pseudo-cell all the gold atoms would have to lie in two parallel planes which are normal to the *b* axis and separated by $\frac{1}{2}y$. In order to derive the real cell it was merely necessary to move the gold atoms from these ideal positions by a small displacement along the *y* axis, which was first determined approximately by trial-and-error methods. The parameters so obtained were then used to work out the signs of the F'_{0kl} coefficients, and a Fourier projection on the *a* plane was calculated (Fig. 3). The position of the gold peak on this projection indicates the magnitude of the shift from the layer plane to be

FIG. 3.

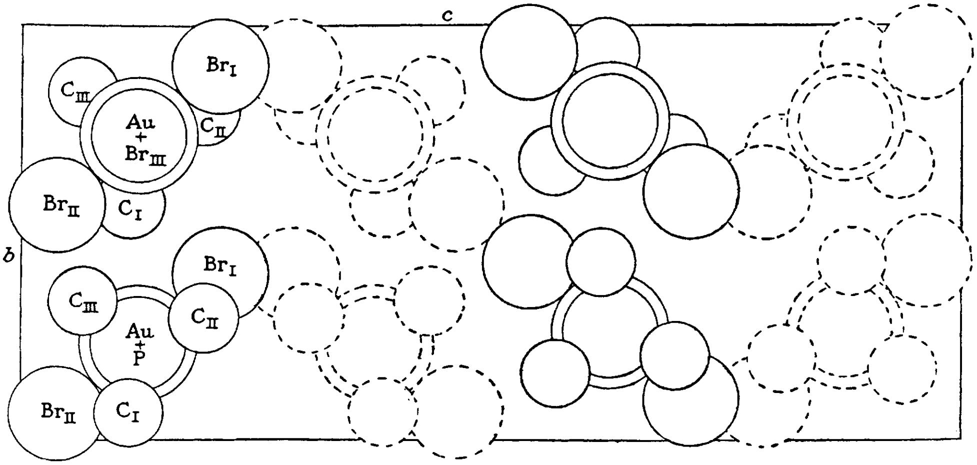


Relative electron-density projection on (100), *showing one quarter of the unit cell. Contours and scale as in Fig.* 1.

0·017y, and the angle between z and the plane of the molecules to be 41°, parameters which gave good agreement between observed and calculated structure amplitudes (Table I*b*). It was noticed that all the observed values of F'_{0k0} considerably exceed the calculated ones; this effect was attributed to reduced absorption in the case of the 0*k*0 reflections, due to the plate-like character of the crystals. If the intensities of all 0*k*0 reflections are scaled down by a common factor, agreement between observed and calculated structure amplitudes of these can be obtained. The general arrangement of the molecules in the *a* projection is illustrated in Fig. 4.

It should be noted that it is impossible, on the basis of either the *a* or the *b* projections, to distinguish between two arrangements of the molecules which appear identical when viewed in projection, but are very different from each other in space. In one case the molecules are placed at $y = \frac{1}{4} \pm 0{\cdot}017$ and $y = \frac{3}{4} \pm 0{\cdot}017$, while in the other case they come to lie at $y = \pm 0{\cdot}017$ and $y = \frac{1}{2} \pm 0{\cdot}017$; this implies a choice between the alternatives of either making the phosphine groups of all the molecules within any one layer point in the same direction, and of reversing their orientation on passing from one layer to the next, or of making every other pair of molecules within the *same* layer point in opposite directions. In order to decide between these two structures an equi-inclination Weissenberg photograph of the 3*kl* reciprocal lattice plane was taken. A comparison of the observed intensities with those calculated on the basis of the two alternative structures led to the conclusion that the first set of parameters mentioned above is the correct one, *i.e.*, that the phosphine groups of all the molecules lying within the same plane point in the same direction. Agreement between observed and calculated structure amplitudes was generally satisfactory, as shown in Table I*c*, and provided additional support for the correctness of the structure.

FIG. 4.



Unit cell projected on (100). *Full circles represent atoms at the height* x, *dashed circles represent atoms at* x + ½. *The molecules are here seen end-on, with the* Br$_{III}$*'s in the top layer and the phosphine groups in the bottom layer pointing towards the observer.* (1 *cm.* = 2 A.)

TABLE II.

Atomic parameters and interatomic distances.

	Parameters.			Intramolecular distances, A.		Intermolecular distances, A.	
	x.	y.	z.				
Au	0·250	0·267	0·125	Au–Br	$2{\cdot}5_0$	C$_{I}$–Br$_{II}$	$3{\cdot}6_1$
Br$_{I}$	0·250	0·101	0·212	Au–P	$2{\cdot}5_0$	C$_{I}$–Br$_{III}$	$3{\cdot}5_5$
Br$_{II}$	0·250	0·433	0·038	Br$_{II}$–C$_{I}$	$3{\cdot}8_4$	C$_{III}$–Br$_{II}$	$3{\cdot}4_5$
Br$_{III}$	0·026	0·267	0·125	Br$_{I}$–C$_{III}$	$3{\cdot}5_6$	C$_{III}$–Br$_{III}$	$3{\cdot}5_6$
P	0·526	0·267	0·125	Br$_{III}$–C$_{I}$	$3{\cdot}5_5$	C$_{II}$–Br$_{II}$	$3{\cdot}4_3$
C$_{I}$	0·625	0·431	0·119	Br$_{II}$–C$_{II}$	$4{\cdot}1_0$	C$_{II}$–Br$_{II}$	$3{\cdot}6_1$
C$_{II}$	0·625	0·197	0·193			C$_{II}$–C$_{I}$	$3{\cdot}4_8$
C$_{III}$	0·625	0·172	0·065				

To locate the positions of the methyl groups a model of the structure was built; it was assumed that the co-ordination around the phosphorus atom is tetrahedral, and the carbon–phosphorus distance is 1·87 A. The need for avoiding an unduly close approach between any pair of methyl groups and bromine atoms made it possible to define the orientation of the phosphine groups within comparatively narrow limits. The most probable carbon positions were finally calculated by rotating the phosphine groups until all C–Br distances were as nearly as possible equal; they are indicated in Table II, which shows the prominent interatomic distances as well as the final co-ordinates of the atoms in the unit cell; the methyl groups are also shown in the drawings of the structure in Figs. 2 and 4.

Conclusions.—Crystals of PMe_3–$AuBr_3$ possess a layer structure. The layers lie normal to the *b* axis and are slightly less than 5 A. apart. The long axis of the molecules is parallel to the *a* axis, with the phosphine groups of all the molecules within any one layer pointing in the same direction; this orientation is reversed on passing from one layer to the next. The bromine atoms are arranged at three corners of a square which has the gold atom as its centre and is inclined at 41° to the plane of the layers. The gold–bromine distance, 2·5 A., is slightly smaller than that found by Burawoy, Gibson, Hampson, and Powell (*loc. cit.*) in their preliminary structure analysis of diethylmonobromogold. The structure is of the same general type as those of four-co-ordinated gold and palladium compounds described by previous investigators (see, *e.g.*, Mann and Wells, *J.*, 1938, 702; Wells, *Proc. Roy. Soc.*, 1938, A, **167**, 169) and provides further support for the square co-ordination of the four covalencies in compounds of auric gold.

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