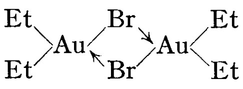
353. *The Constitution of Diethylmonobromogold and Di-*n*-propylmonocyanogold.*

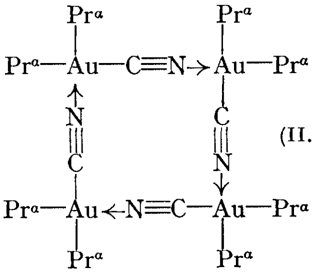
By A. Burawoy, C. S. Gibson, G. C. Hampson, and H. M. Powell.

The dipole moments of diethylmonobromogold and di-*n*-propylmonocyanogold have been accurately determined in carbon tetrachloride solution. These two symmetrically constituted compounds have small but definite dipole moments. The crystallographic examination of diethylmonobromogold shows that the atoms and groups attached to a tervalent and quadricovalent gold atom are coplanar with the gold atom.

The symmetrical constitutional formulæ assigned to diethylmonobromogold (I) and di-*n*-propylmonocyanogold (II) have been based on molecular-weight determinations (Gibson and co-workers, J., 1930, 2531; 1934, 860; 1935, 219) and are in agreement with our knowledge of electronic structure. Apart from its being the first organo-gold compound



(I.)



(II.)

to be isolated (J., 1907, **91**, 2061), compound (I) is the simplest of the series, and compound (II) is of a more complicated type to which a certain interest is attached. Being both colourless and soluble in non-polar solvents, they lend themselves to physical investigation.

The dielectric constants were measured in a platinum-plated condenser of design similar to that described by Jenkins and Sutton (J., 1935, 609). The following results were obtained for solutions in carbon tetrachloride at 25°, the symbols having their usual significance.

Diethylmonobromogold.

f_2.	*d*.	*e*.	n^2.	P_2.	$_{E}P_2$.
0·006259	1·6044	2·2498	2·14310	126·6	89·8
0·004102	1·5975	2·2417	2·13976	126·6	90·7
0·0	1·5844	2·2264	2·13289	—	—

$_{A+O}P_2 = 126{\cdot}6 - 90{\cdot}3 = 36{\cdot}3$ c.c. $\mu = 1{\cdot}32$ D.

Di-n-*propylmonocyanogold.*

f_2.	*d*.	*e*.	n^2.	P_2.	$_{E}P_2$.
0·0063886	1·6026	2·2551	2·14703	249·7	204·3
0·0058538	1·6012	2·2528	2·14615	249·7	204·9
0·0	1·5847	2·2266	2·13289	—	—

$_{A+O}P_2 = 249{\cdot}7 - 204{\cdot}6 = 45{\cdot}1$ c.c. $\mu = 1{\cdot}47$ D.

Since the electron polarisation of the first compound previously found (J., 1935, 221) in benzene is different from that now obtained in carbon tetrachloride, the refractivities were again determined in benzene.

Refractivities of diethylmonobromogold in benzene at 25·0°.

f_2.	*d*.	n^2.	$_{E}P_2$.
0·010514	0·9269	2·27203	90·7
0·006884	0·9086	2·26703	90·7
0·0	0·87355	2·25797	—

The electron polarisation is thus substantially the same in both solvents, and the value of the dipole moment of the compound in benzene previously found is somewhat low.

These substances furnish two more examples of compounds having symmetrical constitutions and possessing dipole moments differing appreciably from zero. The determination of the cause or the explanation of the positive electric moments of symmetrical molecules is still under discussion (see, *e.g.*, papers in *Trans. Faraday Soc.*, 1934, **30**; Sugden, p. 734; H. O. Jenkins, p. 739; Hampson, p. 877; also Hammick, Hampson, and G. I. Jenkins, *Nature*, 1935, **136**, 990; H. O. Jenkins, J., 1936, 862; *Ann. Reports*, 1936, **33**, 133). In view of the fact that many symmetrically constituted compounds having dipole moments of the order of 1 D are known, and their high molecular weights being borne in mind, it must be concluded that the dipole moments of diethylmonobromogold and di-*n*-propylmonocyanogold are in agreement with the symmetrical constitutions (I) and (II) assigned to them.

Preliminary crystallographic investigation of diethylmonobromogold some five years ago having indicated that the bromine atoms and ethyl groups in this compound are coplanar with the gold atoms, it was clear that it is impossible to effect the optical resolution of a 4-covalent and tervalent gold compound having four different atoms or groups attached to the gold atom. The complete investigation of diethylmonobromogold was delayed for a number of reasons, one being the superficial decomposition of the compound by *X*-rays (see below). In the meantime, Cox and Webster (J., 1936, 1635) completed the crystallographic investigation of potassium bromoaurate, $KAuBr_4,2H_2O$, and showed that the four bromine atoms in this salt are coplanar with the gold atom. From this result and that of the crystallographic investigation of diethylmonobromogold, we now know that both in its inorganic and in its organic compounds the tervalent and 4-covalent gold atom exhibits a planar distribution of valencies. The crystallographic investigation has also confirmed the correctness of the constitution assigned to diethylmonobromogold.

Diethylmonobromogold crystallises from ligroin (b. p. 35—40°) in colourless anorthic needles, which are very soft and so easily flexible that normal manipulation of the solution frequently results in bending of the crystals into hook- or loop-shaped forms. The only faces distinguishable with certainty lie along the needle zone and are (100), (010), and $(1\bar{1}0)$. The crystals show extremely high negative double refraction with oblique extinction on all faces and the lesser refractive index always for the ray most nearly along the needle direction.

Oscillation photographs were obtained with a small needle oscillating about the *c* and *b* axes, copper radiation being used. The unit cell dimensions deduced from these are: $a = 9{\cdot}63$, $b = 9{\cdot}33$, $c = 4{\cdot}98$ A.; $\alpha = 121° \, 10'$, $\beta = 89° \, 6'$, $\gamma = 105° \, 48'$, and the density calculated for two molecules of $AuEt_2Br$ is 3·07 g./c.c. There is no evidence from crystal form or pyroelectric effect of the absence of a symmetry centre, and the space group is taken to be $\bar{1}$.

It was impossible to obtain a wholly satisfactory set of photographs for intensity comparisons. The material used shortly after its preparation had darkened slightly, and this superficial decomposition increased under the action of the *X*-rays, the crystals becoming coloured dark violet. Owing to this action and the necessity for setting the crystal by *X*-ray methods, great reliance cannot be placed on the observations. An accurate structure has not been deduced, but sufficient qualitative information has been obtained to suggest the general form of the molecule.

The extreme softness of the crystals and the general appearance of the *X*-ray photographs indicate that a molecular lattice is present. Strong reflexions are obtained at low angles of reflexion, but intensities fall off rapidly with increasing angle θ, showing that there is a large temperature factor diminution. The photographs contrast sharply with those obtained from diethylthallium bromide, which forms a distorted sodium chloride type of structure with $TlEt_2^+$ and Br^- ions and gives strong high-order reflexions.

All arrangements of the atoms within the cell having gold and bromine in special positions without parameters are definitely excluded by irregularities in the main series of reflexions which could not be thus explained. All atoms are therefore in general positions, *e.g.*, Au in xyz, $\bar{x}\bar{y}\bar{z}$; Br in $x'y'z'$, $\bar{x}'\bar{y}'\bar{z}'$. By means of contour diagrams for reflexions $h00$ and $0k0$, the whole range of possible values for x, x', and y, y' was explored, and the parameters limited to a comparatively small region. In making a choice of values the requirements of reflexions $hk0$ were also taken into account. In arriving at these approximate parameters the contributions of the carbon atoms have been ignored since they will be small and, in general, will tend to cancel, but they may have an appreciable influence on the relative intensities of weaker reflexions of small θ value. The parameters z and z' were estimated from consideration of relative intensities of $00l$ for which there are, however, few observations owing to the small spacing, and by use of $h0l$ reflexions, the x and x' values previously found being assumed. Although there are discrepancies in detail, the main variations in intensity are accounted for by the parameters chosen, and the agreement is probably as good as could be expected.

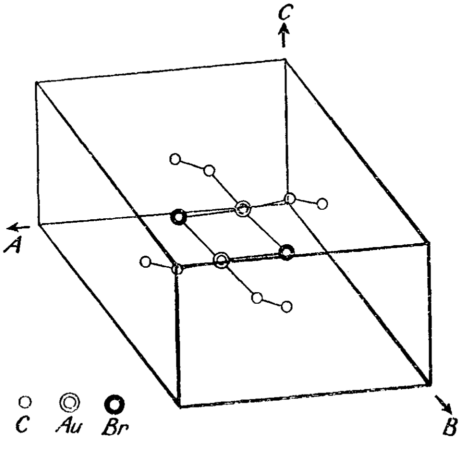
The parameters found are: Au, $x = 0{\cdot}13$, $y = 0{\cdot}125$, $z = -0{\cdot}085$; Br, $x' = 0{\cdot}15$, $y' = -0{\cdot}12$, $z' = 0{\cdot}045$, and calculated and observed relative intensities are given in the table.

	I, calc.	*I*, obs.		*I*, calc.	*I*, obs.		*I*, calc.	*I*, obs.		*I*, calc.	*I*, obs.
100	58	vvs	040	12·4	s—vs	330	1·2	nil	410	7·7	w
200	1·1	m	050	3·9	m—	440	5·2	w	510	0	w
300	23·9	vs	060	2·2	w	$1\bar{1}0$	51·7	vvs	610	4·4	w
400	17·2	s	001	44	vs	$2\bar{2}0$	5·0	ms	120	2·5	s
500	2·3	vw	002	9	vs	$3\bar{3}0$	9·2	s	130	9·4	vs
600	1·1	mw	003	0·2	nil	$4\bar{4}0$	10·0	vs	140	4·3	m
700	4·1	mw	004	0·2	nil	$5\bar{5}0$	2·8	m—ms	111	9·2	s
010	55	vs	110	5·5	nil	210	6·9	s	211	0·8	w
020	0	m	220	2·9	w	310	16·8	ms	311	10	ms
030	11·4	vs									

The orientation of the molecule in the unit cell is indicated in the perspective diagram (Fig. 1) where, for convenience, the origin has been moved to $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$. The molecule projected on the plane of the gold and bromine atoms is shown in Fig. 2. The carbon atoms marked $\oplus$ and $\ominus$ are respectively above and below the plane of the other atoms. The distances marked on Fig. 2 are subject to a probable error of ± 0·1 A.

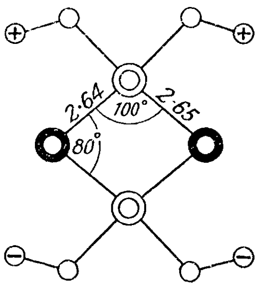
The results show that two gold atoms and two bromine atoms lie close together near the origin and that the molecule is $Au_2(C_2H_5)_4Br_2$. These four atoms form a rough square in a plane somewhat inclined to (001). In order that the molecule may fit into the unit cell, all the atoms must lie approximately in one plane as is shown by the very small *c* dimension, and the four gold valencies must accordingly lie in one plane and will be approximately at right angles to one another.

FIG. 1.



Unit cell and molecule. Origin at ½ ½ ½.

FIG. 2.



With the two ethyl groups attached to each gold atom in this way, the molecule fits into the cell satisfactorily, but probably two of the terminal carbon atoms are slightly above the plane of the rest of the molecule and the other two in corresponding positions below this plane as indicated in the figure, leaving the molecule with a centre of symmetry. This displacement of the terminal carbon atoms is necessary to prevent a too close approach of atoms in adjacent molecules.

The suggested structure is in agreement with the needle habit of the crystals and the very high negative double refraction with the smallest refractive index roughly along the needle direction.

Grants from Imperial Chemical Industries Limited and from the Government Grants Committee of the Royal Society are gratefully acknowledged. One of us (A. B.) is also indebted for a maintenance grant from the Society for the Protection of Science and Learning.

GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON), LONDON, S.E. 1.
THE DYSON PERRINS LABORATORY AND THE MINERALOGY DEPARTMENT,
UNIVERSITY OF OXFORD.

[*Received, August* 30*th*, 1937.]