

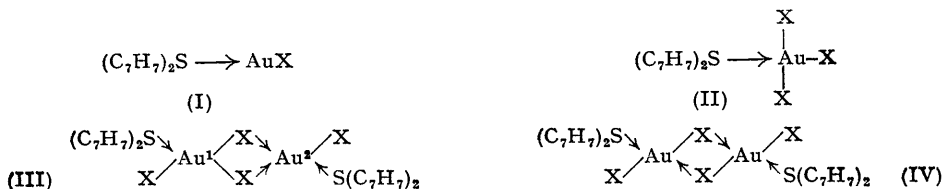
707. *The Nature of Benzyl Sulphide-Dibromo- and -Dichloro-gold.*

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Measurement of molecular weight, electrical conductivity, and magnetic susceptibility has shown that the compound of empirical formula $(C_7H_7)_2S, AuBr_2$ cannot be formulated as a dimer, a salt, or a compound of bivalent gold, and X-ray investigation of the corresponding chloride has shown the presence in the crystal of separate molecules of benzyl sulphide-monochlorogold (I; X = Cl) and benzyl sulphide-trichlorogold (II; X = Cl) so arranged that a highly disordered structure results. From a comparison of the rates of reduction of $(C_7H_7)_2S, AuBr_2$ and benzyl sulphide-tribromogold in chloroform by styrene it is concluded that the former also exists in solution as an equimolecular mixture of the mono- and the tri-bromide (I and II; X = Br).

WHILST there is considerable evidence to show that gold, unlike the other metals of group IB, is unable to exert a valency of two and exists in its compounds only in the univalent (two-covalent) or trivalent (four-covalent) state, the literature contains references to a number of compounds which have been represented as derivatives of the bivalent metal. Such a one is that first isolated by Hermann (*Ber.*, 1905, **38**, 2813) by interaction of ethereal solutions of "auric chloride" and benzyl sulphide, which he formulated as $(C_7H_7)_2S, AuCl_2$ (hereafter referred to as benzyl sulphide-dichlorogold or the dichloride) though its molecular weight (604—608) in boiling chloroform was considerably in excess of the theoretical. Other purely inorganic examples were discussed by Sidgwick ("The Chemical Elements and Their Compounds," Oxford Univ. Press, 1950, p. 177) who considered that they must be complexes containing equal numbers of aurous and auric atoms, though experimental evidence of this has so far only been available in the case of the compounds $CsAuCl_3$, referred to below, and $Cs_2AgAuCl_6$. Unlike most of these compounds, that isolated by Hermann can be recrystallised and was described by him as separating from chloroform in "fiery orange silky needles." The same substance was obtained by Ray and Sen (*J. Indian Chem. Soc.*, 1930, **7**, 67) by mixing chloroform solutions containing equimolecular proportions of benzyl sulphide-monochlorogold (I; X = Cl) and benzyl sulphide-trichlorogold (II; X = Cl). This method of preparation and the fact that the substance reacted with potassium thiocyanate to give potassium aurithiocyanate, $KAu(SCN)_4$, together with (I; X = Cl), which is unaffected by this reagent, convinced them that it was a compound of (I) and (II) (X = Cl). However, their representation of it as $AuCl_3(C_6H_5 \cdot CH_2)_2S, AuCl(C_6H_5 \cdot CH_2)_2S$, though supported by an

observed molecular weight of 944 (theoretical 946) in benzene, did nothing to clarify the mode of compound formation. Such a compound could be formulated in two ways (III and IV; X = Cl. Cf. Gibson, Presidential Address, Section B, British Association, 1938) in which the two gold atoms are united by halogen bridges as in diethylbromogold (Burawoy, Gibson, Hampson, and Powell, *J.*, 1937, 1690). In (III) Au¹ is trivalent with an effective atomic number (E.A.N.) of 86 and Au² is univalent with E.A.N. 84, whilst



in (IV) both gold atoms are bivalent with E.A.N. 85, each therefore having one unpaired electron. It appears from the work of Dohie, Llewellyn, Wardlaw, and Welch (*J.*, 1939, 426) that the valencies of four-covalent aurous gold are coplanar and, if that is so, resonance would be possible in the bridge system of (III).

Smith (*J. Amer. Chem. Soc.*, 1922, **44**, 1769) prepared the analogous dibromide, di-iodide, and iodochloride and discussed the possibility that these and the dichloride might be salts (V; X = halogen) in which the cation contains a univalent and the anion a trivalent gold atom. However, failing to find any increase in the electrical conductivity of an alcoholic solution of (I; X = Cl) on progressive addition of benzyl sulphide, he concluded that (VI; X = Cl) was incapable of existence and that hence the dichloride



was not to be formulated as (V; X = Cl) which has the same cation as (VI). It has now been shown that salts of type (VI) can be prepared, providing X⁻ is an anion of low polarisability, by the interaction of benzyl sulphide-monobromogold (I; X = Br) and benzyl sulphide in an inert solvent with the appropriate solid silver salt. From the nitrate and the perchlorate (VI; X = NO₃⁻ and ClO₄⁻ respectively), which were isolated in this manner, one molecule of benzyl sulphide was displaced by one equivalent of the polarisable bromide or chloride ion to regenerate the non-ionic aurous complex (I; X = Br or Cl respectively). Whilst therefore Smith's conductivity experiments referred to above did not establish beyond doubt the non-existence of salts of type (V), his observation that the dichloride itself was non-conducting in chloroform solution showed a salt-like structure to be unlikely. This is supported by a similar finding by Ray and Sen (*loc. cit.*) that the acetone solution of the same compound is non-conducting when first prepared although it slowly acquires an increasing conductivity, presumably owing to decomposition.

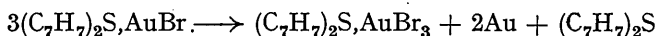
In the present work, incidental to which a further compound of the same type—benzyl sulphide-bromoiodogold, (C₇H₇)₂S.AuBrI—has been isolated, the dibromide has been re-investigated both in the solid state and in solution, and the dichloride and the dibromide have been subjected to X-ray examination. The evidence described below indicates that these substances neither contain bivalent gold nor are true compounds of types (I) and (II) but that they are lattice compounds in the solid state in which, as also in solution, (I) and (II) exist as separate discrete entities. Since the compounds all melt at about 130° with gross decomposition a thermal investigation was not possible.

Molecular Weight.—The molecular weights of the dihalides, determined cryoscopically in bromoform (method of Roberts and Bury, *J.*, 1923, **123**, 2037), or in benzene, are the same as the formula weights. This does not distinguish between true dihalides and substances composed of equimolecular proportions of types (I) and (II), but does show the observations by Hermann and by Ray and Sen to be in error and provides further evidence that the compounds under consideration cannot be (III or IV; X = Br, Cl).

Electrical Conductivity.—Solutions of the same compounds in nitrobenzene have been found to be non-conducting, which confirms the observations by Hermann and by Ray and Sen and their conclusions that the dihalides are not ionic compounds.

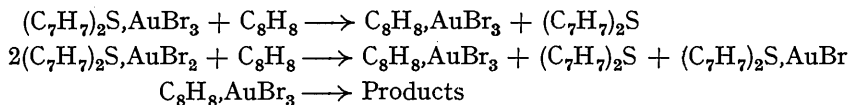
Magnetic Susceptibility.—In consequence of the odd atomic number of gold, compounds containing one atom of this element in which it exerts a valency of two must of necessity contain an odd number of electrons and hence be paramagnetic. Elliott (*J. Chem. Phys.*, 1934, 2, 419) has made use of this to show that the black crystalline compound of empirical formula CsAuCl_3 cannot contain bivalent gold since it is diamagnetic ($\chi = -0.25 \times 10^{-6}$ e.m.u.), concluding that it must be a lattice compound of CsAuCl_2 and CsAuCl_4 , as was later confirmed by Elliott and Pauling (*J. Amer. Chem. Soc.*, 1938, 60, 1848). An examination of benzyl sulphide-mono-, di-, and tri-bromogold by the Gouy method has revealed that these are all diamagnetic in the solid state with $\chi = -0.48$, -0.33 , and -0.36×10^{-6} e.m.u. respectively, but little greater than the value quoted above and that of -0.23×10^{-6} e.m.u. reported by Burawoy and Gibson (*J.*, 1935, 218) for Au_2Br_6 , showing conclusively the absence of bivalent gold from the solid dibromide.

Rate of Reduction in Solution.—Benzyl sulphide-di- and tri-bromogold are reduced by acetone or styrene with or without chloroform as solvent, and this reaction has been investigated kinetically in an attempt to show some difference in behaviour of the two compounds. For this purpose acetone was unsatisfactory (a) because the reaction came to equilibrium (colourless acetone solutions of benzyl sulphide-monobromogold containing hydrogen bromide and monobromoacetone slowly developed the colour characteristic of the di- or tri-bromide) and (b) because of the production of free acid, the catalytic effect of which on the halogenation of acetone is well known, and of bromide ion which is known to influence the rate of somewhat similar reactions, e.g., the disproportionation of benzyl sulphide-monobromogold :



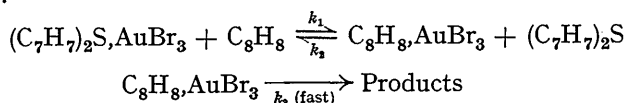
Styrene was therefore selected as reducing agent. In chloroform solution containing a large molecular excess of styrene, benzyl sulphide-tribromogold was reduced smoothly and completely according to the first-order law, the rate being proportional to the styrene concentration over the range investigated.

Parallel experiments were performed under identical conditions at two temperatures with solutions containing twice the molecular concentration of benzyl sulphide-dibromogold [taken as $(\text{C}_7\text{H}_7)_2\text{S},\text{AuBr}_2$] as of benzyl sulphide-monobromogold, i.e., containing the same initial concentration of tribromo-compound in each case on the assumption that the dibromide existed as mono- and tri-bromide in solution. The concentrations of styrene were adjusted according to the conditions to give reasonable rates of reduction, and the progress of the reaction was followed by titrating aliquot portions with sodium thiosulphate solution as described in the Experimental section. At each temperature, in the plot of log titre against time the points for both compounds lie about the same straight line, the results of typical experiments being illustrated in Fig. 1. Thus the solution of the dibromide behaved exactly as would be expected of a solution containing equivalent amounts of mono- and tri-bromide, the activation energy of the reduction hence being the same in each case. Before accepting this evidence of the non-existence of benzyl sulphide-dibromogold in solution it must not be overlooked that the same results would have been obtained if, in the presence of so large an excess of styrene, the benzyl sulphide had been displaced from each compound to give, as common intermediate, a styrene complex of which the rate of further reaction was that measured in each case, e.g. :



This possibility, however, was rejected since the addition of a few drops of styrene to a chloroform suspension of tribromogold, which would be expected to cause reduction at a rate roughly comparable with, and in any case, in view of the insolubility of tribromogold, not greater than, that for benzyl sulphide-tribromogold, resulted in the *immediate* reduction of the compound to metallic gold. If such a styrene complex were formed as an unstable intermediate, as further evidence suggested was indeed the case, it would therefore not be

expected that its further decomposition would be the rate-determining stage of the reaction. That such an intermediate is formed is supported by the further observation that the addition of small amounts of benzyl sulphide to the reaction mixture caused the rate of reduction of benzyl sulphide-tribromogold to fall, clearly indicating that in one stage of the reaction benzyl sulphide is disengaged reversibly. The effect was quantitatively the same on the rate of reduction of the dibromide (Fig. 2). The stages of the reactions are therefore considered to be :



in which the overall rate of reduction would be determined by the rate of formation of the styrene complex; that being so, it is difficult to escape the conclusion that the reactions

FIG. 1. Reduction by styrene at 25° (I) and at 35° (II) of equivalent amounts of benzyl sulphide-tribromogold \bullet and \circ , and benzyl sulphide-dibromogold \odot and Δ .

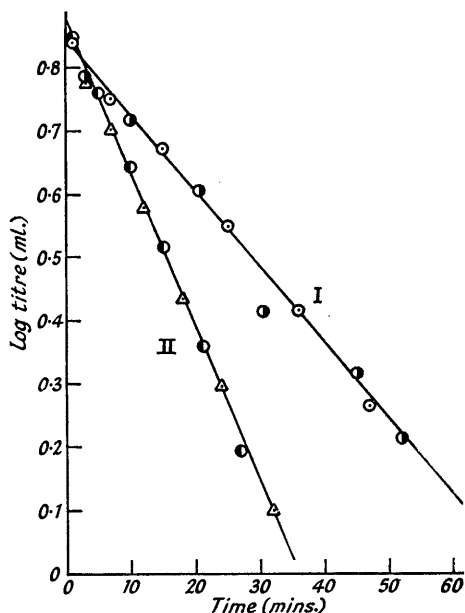
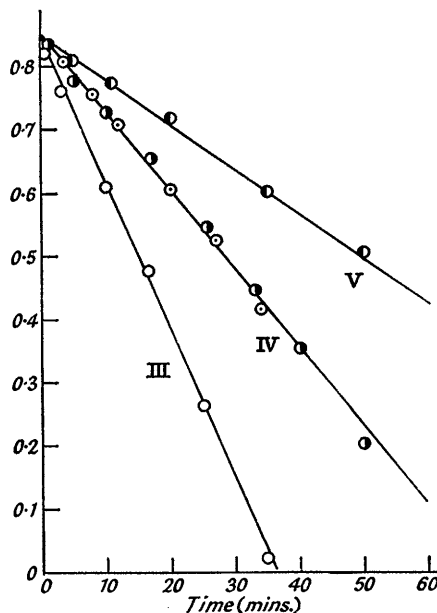


FIG. 2. Effect on reaction rate of added benzyl sulphide : III, nil; IV, 0.1 g.; V, 0.5 g. Benzyl sulphide-tribromogold: \odot , \circ . Benzyl sulphide-dibromogold: \bullet , \circ .



are identical with the two compounds and that therefore solutions of the "dibromide" contain equimolecular amounts of benzyl sulphide-mono- and tri-bromogold. The above mechanism leads to the expression :

$$v = (k_1 k_3 [\text{C}_8\text{H}_8] [(\text{C}_7\text{H}_7)_2\text{S}, \text{AuBr}_3]) / (k_2 [(\text{C}_7\text{H}_7)_2\text{S}] + k_3)$$

for the overall rate of reaction, which, for constant concentrations of styrene and benzyl sulphide, reduces to a first-order relation. It is clear therefore that benzyl sulphide cannot accumulate in the reaction mixture but must rapidly reach a steady value, as would be accounted for by its recombination with aurous bromide, resulting from the reduction, to give benzyl sulphide-monobromogold which is not susceptible to further attack by styrene.

Hitherto, no evidence has been provided for the existence even momentarily of compounds of gold with unsaturated hydrocarbons, but such compounds of ethylene with platinum halides are well known and it is interesting that the electronic configuration of platinum in these and of gold in the styrene complex, the existence of which is postulated above, would be identical, on the assumption that the method of linkage of the unsaturated hydrocarbon is the same in each case.

X-Ray Investigation.—The constitutions of the compounds $(C_7H_7)_2SAuCl_2$ and $(C_7H_7)_2SAuBr_2$ have been found from the examination of their crystal structures. The two compounds form related structures but are not isomorphous. For the chloride the apparent monoclinic unit cell dimensions are $a = 5.66$, $b = 19.79$, $c = 13.39$ Å, $\beta = 92^\circ$. The density is 2.1 g./c.c. and the unit cell contains atoms corresponding to four times the

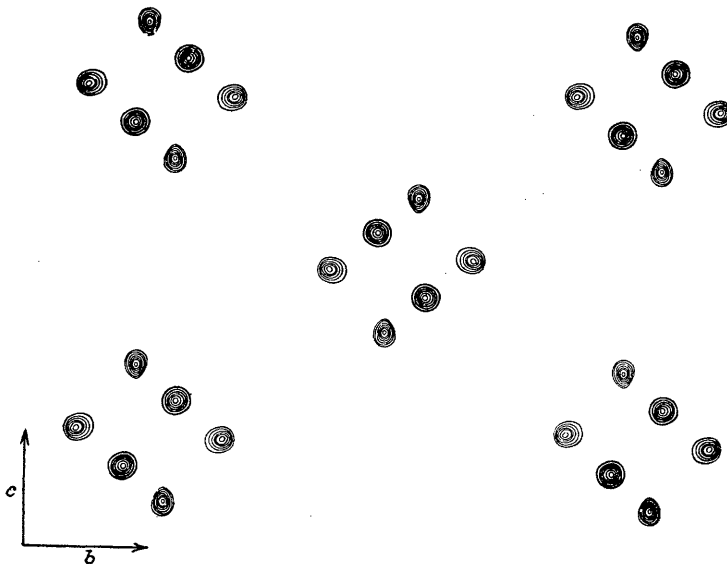


FIG. 3. *Electron-density peaks shown only in the regions of the linear Cl-Au-S groups. The central gold atoms have contours at intervals twelve times those used elsewhere.*

formula stated. With indices based on this cell the absent spectra $0k0$ for k odd and $h0l$ for l odd are those of $P2_1/c$. In this space-group the four gold atoms per unit cell could lie either at centres of symmetry in two sets of equivalent point positions of two-fold

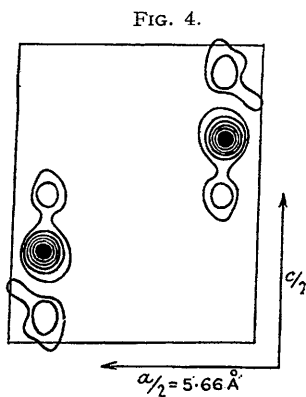


FIG. 4.

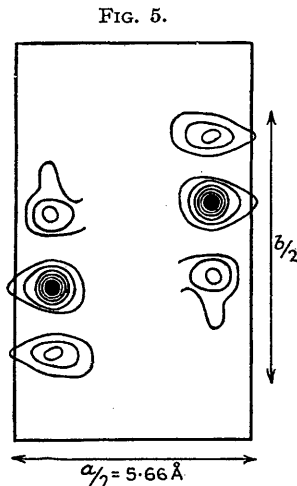


FIG. 5.

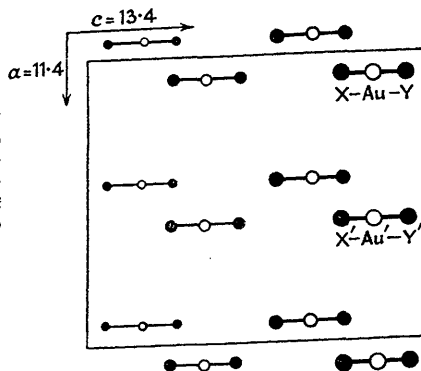
FIGS. 4. and 5. *Electron-density peaks shown only in the region of the linear Cl-Au-S groups.*

multiplicity or in the general point positions of four-fold multiplicity with co-ordinates : xyz ; $\bar{x}\bar{y}\bar{z}$; $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$; $x, \frac{1}{2} - y, \frac{1}{2} + z$. The first of these possibilities, which need not be rejected on any uncertain chemical grounds, requires a set of structure factors entirely at variance with the observed F_{hko} , F_{h0l} , and F_{0kl} values, but consistent values of xyz for gold atoms in the general positions may be readily obtained by F^2 and F Fourier

synthesis in three independent projections. With the co-ordinates then found the main characteristics of the observed F values are reproduced in approximate calculated values which take into account only the gold contributions.

In accordance with the space-group symmetry the four gold atoms would be in every way equivalent and each could therefore be the central atom of a molecule $(C_7H_7)_2SAuCl_2$, but any formula such as $\{(C_7H_7)_2S\}_2Au^+AuCl_4^-$ designed to avoid bivalent gold by the introduction of two dissimilar gold atoms would be impossible. Thus not merely the conclusions drawn from unit cell and space-group symmetry, but also a determination of the co-ordinates for the gold atoms, seem to indicate that the compound contains bivalent gold. This conclusion, however, is false and it arises from a combination of accidental circumstances which are revealed when attempts are made to determine the structure in greater detail. In order to establish the existence of bivalent gold it is necessary to determine the positions of the sulphur and the two chlorine atoms supposedly attached to the gold. Failure of the subsequent stages of the Fourier analysis to reveal more than two of the required atoms led to a re-examination of all the assumptions made and to further X-ray examination with prolonged exposures. It was thus found that the structure must be based on a unit cell of double the a dimension with eight molecules per unit cell. This is shown in X-ray photographs taken with the crystal oscillating about the a axis where, in positions corresponding to a cell of twice the a dimension, there are faint diffuse spots

FIG. 6. Arrangement of the eight gold atoms in the unit cell. Alternate $>S\cdot AuCl$ and $>S\cdot AuCl_2$ molecules lying in the same row parallel to the a axis are indicated by circles of the same size, and the differences in circle size are intended to convey that molecules in the four rows illustrated do not lie at the same depth within the cell.

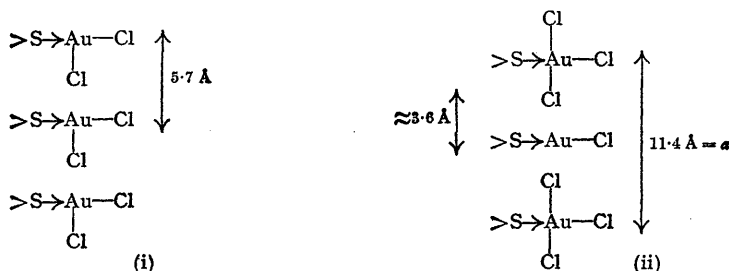


elongated along the layer lines to such an extent that the layer lines are marked by a nearly continuous though not uniform region of darkening of the film. This diffuseness, due to disorder in the structure as discussed below, combined with the weakness of the reflections tends to conceal these effects. All reflections on the other layer lines are sharp. X-Ray examination of the bromide crystals reveals differences which complicate a direct comparison of the two structures but the bromide has a similar short pseudo-cell spacing of 5.7 Å. Intermediate diffuse layer lines, stronger than those of the chloride, indicate a similar doubling of the cell in this direction. In what follows all indices refer to the cell with $a = 11.32$ (chloride). They differ from those relating to the pseudo-cell $a = 5.66$ only in the doubling of h . The sharp reflections have, as before, the systematic absences of $P2_1/c$. The further absences of $h00$, $h0l$, and $hk0$ for h odd do not arise from space-group symmetry but from similarities in co-ordinates of different atoms.

The eight gold atoms of the cell consist of two sets of four atoms in the general positions, $4Au$ in xyz and its equivalents, $4Au'$ in $x'y'z'$ and its equivalents. To account for the pseudo-cell $y = y'$, $z = z'$, and $x = \frac{1}{2} + x'$ must hold. Similar relations hold for the two atoms attached to gold. In each of the three electron-density projections the peaks corresponding to these atoms, e.g., sulphur and one of the chlorine atoms in the case of the dichloride (Figs. 3, 4, and 5), are seen to be in a straight line and these three atoms must therefore form a *linear* group. The absence of peaks high enough to represent the other chlorine atoms is discussed below. Satisfactory positions for the benzyl groups may be inferred from space considerations but since they do not affect the present argument they are not considered here. The arrangement of the eight X-Au-Y groups in the cell is shown in Fig. 6.

The projections derived from observed F_{h0l} and $F_{h\bar{k}0}$ necessarily have the pattern repeating by translation at $a/2$ (5.7 Å) and cannot distinguish atoms of types Au and Au'. This is because the terms with h odd cannot be included, there being no sharp reflections to correspond, and no further progress is possible with these projections. In the third projection F_{0kl} values alone are used; there is no such omission of terms and, in principle, all atoms could show up separately; but in this projection there is a complete atom-for-atom overlap of X-Au-Y and X'-Au'-Y'. Here also, but for a different reason, the presence of the two groups of atoms cannot be demonstrated. Three-dimensional Fourier analysis which could resolve the difficulty cannot be made owing to the impossibility of observing F_{hkl} with h odd, the corresponding spots being diffuse; it is precisely these values of F that would introduce any distinctions between the two groups. In these difficult circumstances it is still possible to determine enough of the structure for the present purpose. This may be done by use of the information of both positive and negative kinds in the projections, and by a comparison of the chloride and bromide.

Although the bromide structure as a whole is somewhat different, the zero layer line Weissenberg photographs for rotation about the 5.7 (pseudo-cell) axis show a marked resemblance, and the corresponding patterns seen in projection have the overlapping X and X' peak about twice as high as that for the overlapping Y and Y'. This can only be so if X and X' are both bromine and Y and Y' are both sulphur atoms. This excludes the possibility that the alternate gold atoms are those of $[(C_7H_7)_2S \rightarrow Au \leftarrow S(C_7H_7)_2]^+$ and $AuBr_4^-$ groups since in such a case each peak would be due to a bromine and an overlapping sulphur atom. In the chloride, where X and Y have approximately the same peak height, there is good resolution of these two atoms attached to each gold but in none of the three projections are there any peaks to represent the second chlorine although there is ample evidence, including the projections themselves, that the observed F's and their calculated signs are substantially correct. The $0kl$ projection is not influenced by the disorder that affects the h indices, and in this case the only possible explanation for the lack of the other chlorine peak is that there is overlapping with the gold atom. This is confirmed in the bromide, where the relative peak heights show that the second bromine atom is similarly concealed by gold. In the other two chloride projections, where the second chlorine does not overlap, the lack of sufficiently high peaks is due to the disorder effect indicated by the diffuseness of the odd h layer lines. That the halogen is involved in the disorder is shown by the greater intensity of the diffuse spots in the bromide. Chlorine atoms are therefore fixed on lines joining Au . . . Au . . . Au and occupy alternative positions in such a way that no position holds statistically more than about $\frac{1}{2}Cl$ and consequently there is no peak comparable with those of sulphur and chlorine. One chlorine atom must be inserted somewhere between each pair of gold atoms, and since even the mid-point is only 2.83 Å from the gold atom this chlorine atom is considerably closer than the separations to be expected for ions or unlinked atoms. It must therefore be linked by a covalency to one atom, at about 2.1 Å. This leaves a satisfactory space of 3.56 Å between it and the other



gold neighbour to which it is not linked. If the structure were represented by the atomic arrangement (i), a disorder effect could be obtained by placing chlorine atoms above instead of below gold atoms in some rows, but the repeat distance along a would be 5.7 Å. Neither the sharp reflections nor the diffuse layer lines corresponding to $a = 11.4$ are explained by this arrangement. They are, however, explained by the structure (ii), in which alternate

gold atoms have valencies 1 and 3. The unit repeat distance is clearly 11.4 Å and the disorder arises through . . Au . . . Au' . . . Au . . rows' being displaced by 5.7 Å along a so that in different unit cells a given point position may be occupied equally well by Au or Au'. In projections which contain the Au . . . Au' . . line every gold atom will therefore have adjacent to it two positions each occupied statistically by $\frac{1}{2}$ Cl. This corresponds in electron density to little more than a CH group and therefore in the presence of benzyl groups does not show up in the same clear manner as the single chlorine atom.

The structure consists of $(C_7H_7)_2SAuCl$ and $(C_7H_7)_2SAuCl_3$ molecules, both of which can be readily formulated in accordance with the common valency behaviour of gold and are known to exist separately. The compound does not contain bivalent gold but is a crystalline molecular compound of these two substances.

EXPERIMENTAL

Unless otherwise stated all the compounds described below melted with decomposition at or about 130°. Analyses were carried out by Drs. Weiler and Strauss, Oxford.

Benzyl Sulphide-Dichlorogold.—This was prepared as described by Hermann (*Ber.*, 1905, 38, 2813) and recrystallised from chloroform containing a little benzyl sulphide. The compound was obtained in the fiery orange needles he describes [Found: Au, 40.8%; *M* (cryoscopic) in benzene, 500; in bromoform, 473. Calc. for $C_{14}H_{14}Cl_2SAu$: Au, 40.9%; *M*, 482]. A solution of the compound in nitrobenzene, examined in a Mullard conductivity apparatus, type E7566, was non-conducting.

Benzyl Sulphide-Monobromogold.—This was prepared from the hydrobromoaurous acid reagent described by Brain, Gibson, and Imperial Chemical Industries Limited (B.P. 497,746). A warm solution of potassium bromoaurate (5 g.) in ethanol (25 ml.) containing a little water was reduced by addition of an ethanolic solution of sulphur dioxide until colourless, and benzyl sulphide (2 g.) in warm ethanol (15 ml.) added at once. A colourless oil separated which rapidly solidified on being stirred. After being cooled thoroughly, the solid was collected, washed with water, dried over concentrated sulphuric acid, and recrystallised by dissolution in chloroform, containing a little benzyl sulphide, on the water-bath, filtration, and addition of ligroin (b. p. 60–80°) until crystallisation set in. Long colourless needles of benzyl sulphide-monobromogold (3.78 g., 91%) slowly separated. These were collected, washed with a 1:1 mixture of chloroform–ligroin (b. p. 60–80°), and dried in air [Found: Au, 40.1%; *M* (cryoscopic) in bromoform, 492. Calc. for $C_{14}H_{14}BrSAu$: Au, 40.1%; *M*, 491]. A solution of the compound in nitrobenzene examined as above was non-conducting.

Benzyl Sulphide-Tribromogold.—Benzyl sulphide-monobromogold (1 g.) in warm chloroform (5 ml.) was treated with bromine in carbon tetrachloride (9.4 ml. of 0.435*N*-solution = 2 equiv.). The resulting deep red solution gradually deposited dark ruby-red crystals (0.9 g., 81%) of benzyl sulphide-tribromogold, which were collected, washed with carbon tetrachloride, and dried in air [Found: Au, 30.0; Br, 36.7%; *M* (cryoscopic) in benzene, 654. $C_{14}H_{14}Br_3SAu$ requires Au, 30.3; Br, 36.8%; *M*, 651]. A solution of the compound in nitrobenzene examined as above was non-conducting.

Benzyl sulphide-dibromogold was prepared somewhat unsatisfactorily by Smith (*loc. cit.*) by the action of benzyl sulphide on an ethereal solution of hydrobromoaurous acid. We obtained it very simply by the method employed above for the tribromo-compound, using one half the proportion of bromine.

Benzyl sulphide-monobromogold (1.36 g.) was dissolved in warm chloroform (10 ml.) and treated with bromine in carbon tetrachloride (3.4 ml. of 0.82*N*-solution = 1 equiv.). The deep red solution rapidly deposited brown needles (1.48 g., 93%) of benzyl sulphide-dibromogold, which were collected, washed with carbon tetrachloride, and dried in air. The compound recrystallised from warm chloroform containing benzyl sulphide, but as prepared was pure [Found: Au, 34.5; Br, 27.6%; *M* (cryoscopic) in bromoform, 584. Calc. for $C_{14}H_{14}Br_2SAu$: Au, 34.5; Br, 28.0%; *M*, 571]. A solution of the compound in nitrobenzene examined as above was non-conducting.

This substance was also obtained by the interaction of benzyl sulphide-mono- and -tribromide in solution in the same way as for the dichloride (Ray and Sen, *loc. cit.*). Benzyl sulphide-monobromogold (0.47 g.) was dissolved in warm chloroform (3 ml.) containing a little benzyl sulphide and mixed with a solution of benzyl sulphide-tribromogold (0.63 g., 1 mol.) in warm chloroform (12 ml.) also containing a little benzyl sulphide. Pure benzyl sulphide-dibromogold (0.75 g.) gradually crystallised, identical in appearance with that obtained as above (Found: Au, 34.5%).

Benzyl Sulphide-Bromiodogold.—A solution of iodine (0.8 g., one equiv.) in chloroform was added to benzyl sulphide-monobromogold (3.8 g.) in chloroform (30 ml.), and the mixture set aside. The almost black crystals (3.9 g.) which separated were collected, washed with a little chloroform, and dried in air. Recrystallisation from chloroform gave pure *benzyl sulphide-bromiodogold* (Found: Au, 32.0; Br + I, 33.6; S, 5.4. $C_{14}H_{14}BrISAu$ requires Au, 31.9; Br + I, 33.5; S, 5.2%).

Di(benzyl sulphide)-Aurous Nitrate.—Benzyl sulphide-monobromogold (2.15 g.) and benzyl sulphide (1.2 g.) were dissolved in warm chloroform (20 ml.) and vigorously shaken in a stoppered bottle with finely powdered silver nitrate (0.75 g.) for 15 minutes. The solution was filtered, the residue washed with a little warm chloroform, and the combined filtrate allowed to evaporate slowly in a dry atmosphere. Colourless transparent prisms (2.12 g.), m. p. 104–107° (decomp.), of *di(benzyl sulphide)-aurous nitrate* separated, which were collected, washed with chloroform, and dried. In the air the crystals became opaque owing to loss of chloroform of crystallisation and when kept they slowly darkened (Found, on freshly prepared material: Au, 24.3; on material dried to constant wt.: C, 48.2; H, 4.2; Au, 28.3. $C_{28}H_{28}O_3NS_2Au, CHCl_3$ requires Au, 24.4. $C_{28}H_{28}O_3NS_2Au$ requires C, 48.9; H, 4.1; Au, 28.7%). This substance was insoluble in water, acetone, and ligroin but dissolved in methanol, ethanol, chloroform, and acetic acid, such solutions depositing gold when heated. Pyridine displaced benzyl sulphide from it in the cold, as did aqueous solutions of potassium bromide and sodium chloride.

The compound (0.5 g.) was shaken with chloroform (5 ml.) and a solution of potassium bromide (0.075 g.) in water (1 ml.) until all had dissolved. The chloroform layer was separated and after being dried (Na_2SO_4) was treated with ligroin (b. p. 60–80°) until crystallisation set in. The crystalline product proved to be benzyl sulphide-monobromogold (0.28 g., theor., 0.30 g.) (Found: Au, 40.0. Calc. for $C_{14}H_{14}BrSAu$: Au, 40.1%).

Repetition of this experiment with an equivalent (0.04 g.) of sodium chloride in place of potassium bromide gave benzyl sulphide-monochlorogold (0.24 g.; theor., 0.28 g.) (Found: Au, 44.1. Calc. for $C_{14}H_{14}ClSAu$: Au, 44.1%).

Di(benzyl sulphide)-Aurous Perchlorate.—This was obtained as described, by the action of solid silver perchlorate (0.4 g.) on benzyl sulphide-monobromogold (0.87 g.) and benzyl sulphide (0.42 g.) in warm chloroform (15 ml.). The perchlorate was somewhat less soluble than the nitrate and it was necessary to extract the insoluble silver salts several times with warm chloroform to remove that part which crystallised out during the reaction. The filtered chloroform solution gave colourless prisms of *di(benzyl sulphide)-aurous perchlorate* (0.57 g.), m. p. 140° (decomp.), on slow evaporation. These, like the nitrate, became opaque owing to loss of chloroform of crystallisation (Found, on freshly prepared material: Au, 23.2; on material dried to constant wt.: Au, 27.2; C, 46.9; H, 4.2. $C_{28}H_{28}O_4ClS_2Au, CHCl_3$ requires Au, 23.3. $C_{28}H_{28}O_4ClS_2Au$ requires Au, 27.2; C, 46.4; H, 3.9%).

Reaction Rate Experiments.—Approx. 10^{-3} mole of benzyl sulphide-tribromogold and exactly twice this amount of the dibromo-compound [*i.e.*, ca. 2×10^{-3} mole taken as $(C_7H_7)_2S_2AuBr_2$] were used for each pair of experiments. The gold compound was dissolved in, and made up to 100 ml. with, chloroform which had been dried over potassium carbonate and redistilled. Commercial styrene was redistilled under reduced pressure and kept in the dark at -5° . The chosen volume of styrene was diluted with the same chloroform to 100 ml. and the two solutions were left in the thermostat for 30 minutes before being mixed. At intervals, 20 ml. of the mixture were withdrawn by pipette and run into 10 ml. of 40% (w/v) aqueous potassium thiocyanate in a stoppered bottle, which was then shaken vigorously for 20 seconds. This stopped the reaction by precipitating the remaining auric gold in the form of a salmon-coloured compound, the nature of which was not investigated. The compound was somewhat soluble in the aqueous phase but sparingly so in the chloroform and the amount of unreduced gold was determined by titration with approx. N/40-sodium thiosulphate, with vigorous shaking after each addition, until all the precipitate had redissolved and the last trace of salmon colour had disappeared from the aqueous layer. Experiment showed that in this titration one molecule of benzyl sulphide-tribromogold required exactly two molecules of thiosulphate.

The authors thank Dr. R. S. Nyholm for making the measurements of the magnetic susceptibilities, and one of them (A. T.) gratefully acknowledges a grant from Imperial Chemical Industries Limited.

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[Received, April 10th, 1952.]