23. *The Organic Compounds of Gold. Part IX. The Structure of Tetraethylsulphatodigold,* $(Et_2Au)_4(SO_4)_2$.

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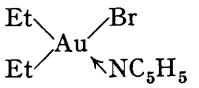
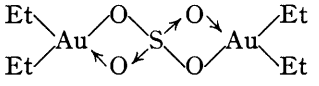
The most probable structure of the compound is deduced and discussed.

PENDING a convenient opportunity for carrying out an *X*-ray investigation of this compound, apparently a polynuclear metallic complex of a novel type, it appears useful to record some considerations regarding its structure.

Any acceptable formula for this compound must incorporate three well-established principles: (i) In a purely covalent complex, each univalent Et_2Au group must be, to acquire stability, the acceptor of a further co-ordinate link, as for example in (I). The necessary co-ordinate links in the sulphato-compound can only be formed by the lone pairs of electrons of the oxygen atoms in the sulphate groups. (ii) The four valencies of each gold atom in the complex must lie in (or nearly in) a plane. (iii) The sulphate groups must be tetrahedral.

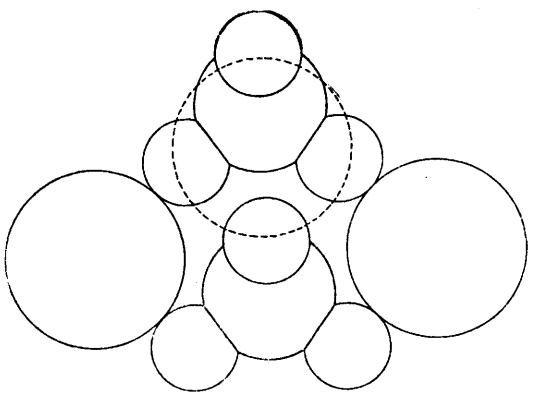
(I.) 



(II.)

Structure (II) would satisfy these conditions, but the observed molecular weight corresponding to double this formula (see preceding paper) renders this inadmissible. It must then be concluded that such a structure containing four-membered rings built up from one large (gold) atom and three smaller ones is unstable.* Calculation, using the observed radii of the atoms (see below), shows that the oxygen valency angle would be 90° and that of the gold atom would be reduced from the natural value of 90° to 70°. It would thus appear that no gold atom can be linked to two oxygen atoms in the same sulphate group.

FIG. 1.



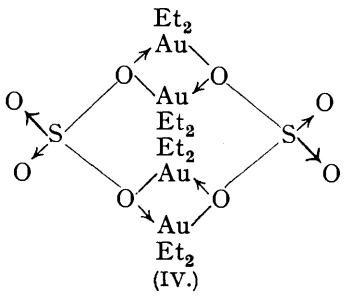
Large circles, gold; medium, sulphur; small, oxygen.

Now the four gold atoms in $(Et_2Au)_4(SO_4)_2$ require altogether the formation of four normal and four co-ordinate links with the oxygen atoms of the sulphate groups. Since these types of links differ only in the distribution of charge, they may, for the moment, be considered as equivalent. The following ways of distributing eight bonds between the eight oxygen atoms are then possible.

(*a*) If each oxygen atom forms only one link, it leads to the structure (III), represented in projection by Fig. 1, with the two sulphate groups in the same orientation, corresponding pairs of oxygen atoms being spanned only by a gold atom. The packing of the sulphate groups is very close. For a gold valency angle of 90° the angle between the oxygen–sulphur and oxygen–gold valency bonds is either 171° or 98°. Considerable distortion is therefore necessary for four of the oxygen valency angles. A more serious objection to this model is that some of the oxygen–oxygen and oxygen–sulphur separations between the two sulphate groups are only about 2·08 and 2·4 A. respectively. Both are thus 0·8 A. less than the sum of the so-called van der Waals radii (see Pauling, "Nature of the Chemical Bond," 1939, p. 176). Such a close approach of two unlinked atoms not themselves linked directly to a third has not been observed.

* Such four-membered rings have not yet been encountered and this point is also dealt with in the preceding paper.

(*b*) It is therefore necessary to assume that four of the oxygem atoms take no part in bond formation with the gold atoms, each of the other four forming two bonds each.*

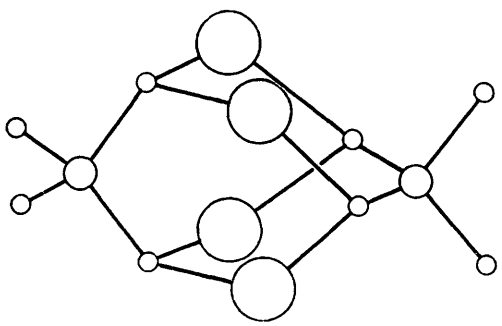


(IV.)

This leads to structure (IV) or (V) (the latter shown in Figs. 2 and 3); the ethyl groups are omitted to make the diagrams clearer. In (IV) four-membered rings again feature, but, unlike those already mentioned, they involve two large gold atoms and are of a type well authenticated when halogen atoms are the bridging groups. The objection to this structure is not in the four-membered rings *per se* but in the resulting separation of the gold atoms in the separate rings, which would only be about 2·5 A. apart, 0·4 A. less than twice the covalent radius of gold.

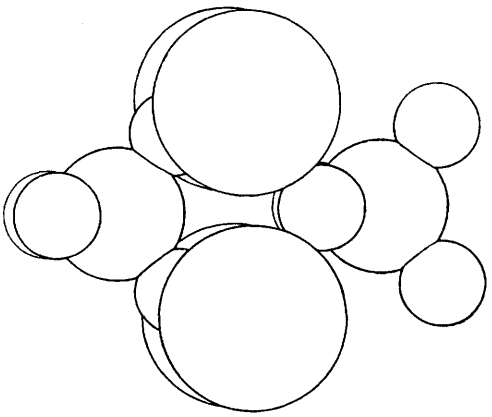
Structure (V) overcomes these difficulties. If the sulphur atom of one sulphate group is chosen as origin, the co-ordinates of the atoms are, from the symmetry of the model, as follows: S (0, 0, 0), (x, 0, 0); O (a, $\pm b$, 0), ($-a$, 0, $\pm b$), ($x + a$, $\pm b$, 0), ($x - a$, 0, $\pm b$); Au ($x/2$, $\pm c$, $\pm c$). Each gold atom

FIG. 2.



Large circles, gold; medium, sulphur; small, oxygen.

FIG. 3.



Large circles, gold; medium, sulphur; small, oxygen.

forms part of a puckered six-membered ring and the symmetry is such that they lie at the corners of a square. The two sulphate groups are similarly oriented in space, so that the four oxygen atoms forming the bonds lie at the corners of a tetrahedron. For calculation the following dimensions were used: Oxygen radius, 0·66 A.; sulphur radius, 1·04 A. (Pauling, *op. cit.*, p. 154); sulphate group tetrahedral with S–O bond 1·51 A. (*idem*, *ibid.*, p. 221); gold radius, 1·43 A.†

With these data it is possible to calculate all the other valency angles and interatomic distances in terms of one parameter x, the distance separating the two sulphur atoms. Parameters a and b are fixed by the dimensions of the sulphate group and c is a function of a, b, and x. The results are summarised:

x, A.	O–Au–O angle.	Au–O–Au angle.	S–O–Au angle.	Au–Au distance, A.
3·6	85° 30′	121° 28′	128° 8′	3·82
4·0	95° 52′	110° 28′	121° 5′	3·43
4·4	108° 37′	100° 16′	122° 2′	3·21
4·8	125° 00′	88° 1′	122° 6′	2·90
5·2	149° 45′	72° 18′	120° 4′	2·47

From these it appears that the most likely model is one in which the corresponding atoms of the two sulphate groups are separated by about 4 A. The natural gold valency angle

* Any distribution of valency bonds between the oxygen atoms which is less symmetrical than in (*a*) or (*b*) leads to most unlikely and unsymmetrical structures.

† Elliott and Pauling (*J. Amer. Chem. Soc.*, 1938, **60**, 1846) find Au–Cl in $AuCl_4$ to be 2·42 A. The radius of Cl being taken as 0·99 A., the radius of Au becomes 1·43 A.

of 90° is then increased only to about 96° and the oxygen valency angles differ little from the usual value. The adjacent gold atoms are then separated by about 3·4 A., *i.e.*, any pair of gold atoms linked to the same oxygen atom is separated by 0·5 A. more than twice the covalent radius of gold.

A model of this structure leads to a very rigid and close-packed assemblage in which the planar distribution of valencies around the gold atoms can be maintained.* The planes containing these sets of four valencies are, however, inclined to that of the square formed by the four gold atoms whose diagonals are rotational axes of symmetry, a rotation of 180° bringing the model into self-coincidence.

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