X-Ray Crystal and Molecular Structure of Au_4Cl_8, the Product of the Reduction of Au_2Cl_6 by Au(CO)Cl

By DANIELA BELLI DELL'AMICO, FAUSTO CALDERAZZO,* FABIO MARCHETTI, and STEFANO MERLINO*
(*University of Pisa, Istituto Chimica Generale and Istituto Mineralogia e Petrografia,* 56100 *Pisa, Italy*)

and GIOVANNI PEREGO
(*Snam-Progetti S.p.A., Direzione Ricerca e Sviluppo,* 20097 *S. Donato Milanese, Milano, Italy*)

Summary The product isolated from the reaction of Au_2Cl_6 with Au(CO)Cl and having the empirical formula $AuCl_2$, is a gold(III)–gold(I) mixed-valence compound with the formula Au_4Cl_8; a crystal structure determination shows that it adopts a chair-like molecular arrangement.

WE reported[1] the isolation of a black substance with the empirical formula $AuCl_2$, obtained by treating anhydrous gold(III) chloride with Au(CO)Cl[2] under an inert atmosphere (nitrogen or argon) in chlorinated solvents, preferably thionyl chloride, at room temperature. This extremely air-sensitive substance has now been studied by *X*-ray crystallographic analysis, which has established its molecular structure as that of a covalently bonded gold(III)–gold(I) mixed-valence compound[3] having the formula Au_4Cl_8. The crystals were grown by allowing a thionyl chloride solution of Au(CO)Cl to react with suspended Au_2Cl_6 at room temperature under diffusion-controlled conditions.

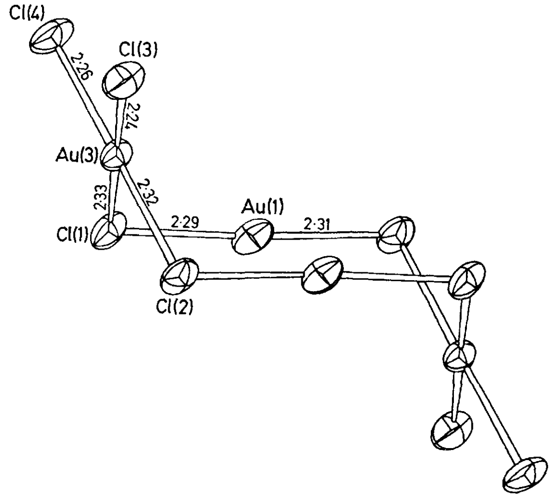

FIGURE. Molecular structure of Au_4Cl_8 with bond distances (Å).

Crystal data: M, 1071·5, triclinic, $a = 7{\cdot}015(4)$, $b = 6{\cdot}830(2)$, $c = 6{\cdot}684(4)$ Å, $\alpha = 94{\cdot}4(1)$, $\beta = 107{\cdot}5(1)$, $\gamma = 88{\cdot}4(1)°$, $U = 304{\cdot}5$ Å^3, $D_c = 5{\cdot}84$ g cm^{-3}, $Z = 1$, space group $P\bar{1}$. Crystals having the dimensions $0{\cdot}9 \times 0{\cdot}06 \times 0{\cdot}015$ mm^3 were used to measure intensities with an automated Siemens AED diffractometer and Zr-filtered Mo-K_α radiation, using the θ—2θ scan method and the 'five points' technique.[4] 1466 reflections were collected; 989 had $I > 3{\cdot}0\,\sigma\,(I)$ [$\sigma^2\,(I)$ = total counts + $(0{\cdot}005I)^2$] and these were used in the structure solution. Absorption corrections were applied[5] assuming an idealised shape. The structure was solved by Patterson and Fourier methods and refined by least-squares methods with anisotropic thermal parameters for all the atoms; the final conventional R value of 0·11 may be regarded as satisfactory in view of the twinning observed along the [001] axis and the poor quality of the crystal.

The structure consists of discrete Au_4Cl_8 molecules, each located on a centre of symmetry with approximately C_{2h} $(2/m)$ symmetry. The molecular arrangement is shown in the Figure together with all the independent bond distances (average standard deviation for the Au–Cl bond distance is 0·02 Å). The gold atoms in the asymmetric units have distinct co-ordination geometries. Au(1) is linearly co-ordinated, the Cl–Au–Cl angle (175·0°) being close to the ideal value. Au(3) has a slightly irregular planar four co-ordination, the Au–Cl_{br} distance (2·33 Å) being somewhat longer than the Au–Cl_t distance (2·24 Å), as expected and found[6] for Au_2Cl_6; the four Cl–Au(3)–Cl bond angles do not deviate essentially from 90°. The Au(3)–Cl and Au(1)–Cl bond distances in this molecule compare quite well with those found in Au_2Cl_6[6] and AuCl,[7] respectively. It is interesting to note that the distance between the two Au(1) atoms is 3·095 Å, compared with 2·884 Å in the metal[8] and 2·98 Å[9] and 3·02 Å[10] for the Au–Au mean distances between peripheral Au atoms in some clusters. The atoms Cl(1), Cl(2), Au(1) and those related by symmetry are coplanar. It is interesting to compare the Au(1)–Au(1) distance with that between Cl(1) and Cl(2) (3·28 Å). Both the short Au(1)–Au(1) distance and the deviation from linearity in the Au(1) co-ordination clearly indicate a bonding interaction between the two symmetry-related Au(1) atoms. This, together with the possible Au(3)–Au(1) orbital interaction may be responsible for the deep colour of the substance.

The existence of a compound with the composition $AuCl_2$ has been the subject of debate in the literature.[11] It should be stressed that the isolation of Au_4Cl_8 is believed to be possible only under the mild and controlled conditions used in the present study. Phosgene is the oxidation product of co-ordinated CO in the reaction of $AuCl_3$ with Au(CO)Cl in a 3 : 1 molar ratio. This, and the spectroscopic identification[1] of an unstable soluble carbonyl species of probable formula $Au_2(CO)Cl_4$, similar to the olefin mixed-valence complexes reported by Hüttel and his co-workers,[12] suggest that the formation of Au_4Cl_8 can be best represented by equation (1). The relevance of these facts to the problem of the reduction of anhydrous metal halides by CO, and of the transient existence[13] of M–COCl bonds, is noteworthy.

$$Au_2(CO)Cl_4 + Au_2Cl_6 \rightarrow COCl_2 + Au_4Cl_8 \qquad (1)$$

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