Insertion of Carbon Disulphide into a Metal–Chlorine Bond; *X*-Ray Structure of $AuCl_2(\eta^2\text{-}S_2CCl)$

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The reaction of CS_2 with gold(III) chloride (Au_2Cl_6) leads to the complex $AuCl_2(\eta^2\text{-}S_2CCl)$, in which the CS_2 has inserted into an Au–Cl bond of a hypothetical monomeric gold(III) trichloride intermediate; the structure has been confirmed by *X*-ray crystallography, although the S and Cl atoms could not be distinguished.

Insertion reactions of CS_2 into M–C and M–N bonds are well known and many examples can be found in standard texts.[1] We have now found that CS_2 can insert into an Au–Cl bond of gold(III) chloride to form a complex $AuCl_2(\eta^2\text{-}S_2CCl)$ containing a chlorodithioformate ligand. As far as we are aware, both the insertion mode and the ligand have been unknown until now.

Gold(III) chloride (0.1 mmol Au_2Cl_6) was dissolved in 20 ml carbon disulphide, giving a red solution that gradually became orange on refluxing. After 30 min, some yellow AuCl was

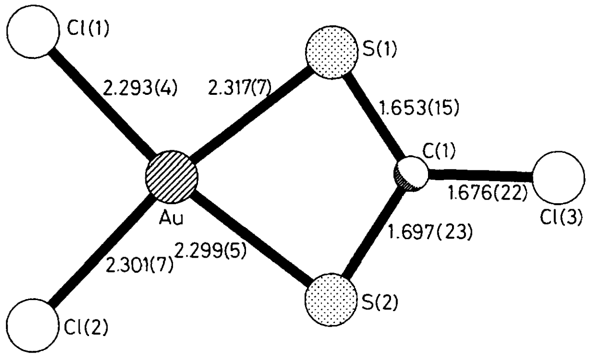

Figure 1. The molecule of $AuCl_2(\eta^2\text{-}S_2CCl)$ in the crystal, showing the atom numbering scheme. Radii are arbitrary. Bond lengths are given in Å.

filtered off and the solution concentrated, whereupon orange crystals formed (yield 60%; satisfactory full elemental analysis was obtained for the composition $AuCl_3{\cdot}CS_2$). Owing to their limited stability in air, the crystals were sealed in glass capillaries for *X*-ray measurements.†

The structure of the product $AuCl_2(\eta^2\text{-}S_2CCl)$, as established by the *X*-ray study, is shown in Figure 1.‡ The molecule is planar (mean deviation of all atoms 0.007 Å), as would be expected for Au(III), but the bite of the S_2CCl ligand is too small to allow ideal angles at the metal atom [S(1)–Au–S(2) 75.0(2)°; the S–C–S angle is also narrow at 114(1)°]. The C–S bond lengths correspond to the expected bond order of 1.5. Other bond lengths and angles are essentially normal, although only two structures with S_2Cl_2 co-ordination spheres at gold are available for comparison: *cf.* Au–S 2.303, 2.314; Au–Cl 2.307, 2.314(2) Å in $[AuCl_2(SPPh_2NPPh_2S)]$[2] and Au–S 2.264—2.274(4); Au–Cl 2.307—2.319(4) Å in two molecules of $[Cl_2Au(C_4H_6S_4)]$;[3] the short Au–S bond lengths in the latter complex may be a consequence of the lack of chelate ring strain (S–Au–S 90.7°) or of the radical anion ligand.

Gold(III) chloride is dimeric; ligands such as pyridine are capable of breaking the chloride bridges to form monomeric adducts $LAuCl_3$. It is therefore reasonable to suggest that CS_2 reacts initially in a similar manner to form an intermediate (σ-$SCSAuCl_3$), with the free S atom then inserting into a Au–Cl bond. However, we have not tested this hypothesis.

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† *Crystal data*: $CAuCl_3S_2$, M = 379.5, monoclinic, space group $C2/c$, a = 14.895(5), b = 10.325(3), c = 10.765(3) Å, β = 120.19(2)°, U = 1431 Å^3, Z = 8, D_x = 3.52 g cm^{-3}, $F(000)$ = 1344, λ(Mo-K_α) = 0.71069 Å, μ = 22.1 mm^{-1}. Orange prism, 0.24 × 0.12 × 0.08 mm. 3801 Profile-fitted intensities[4] were measured on a Stoe–Siemens four-circle diffractomer. Merging equivalents gave 1261 unique reflections (R_{int} 0.050), of which 881 with $F > 4\sigma(F)$ were used for all calculations (program system SHELX, modified by its author Prof. G. M. Sheldrick). Absorption corrections based on ψ-scans gave transmission factors 0.87—0.95. Cell constants were refined from 2θ values of 35 reflections in the range 20—23°. The structure was solved by the heavy-atom method and subjected to full-matrix least-squares refinement on F. The final R value was 0.060, with R_w 0.047. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003F^2$. 64 Parameters, S 1.5, max. Δ/σ 0.001, max. $\Delta\rho$ 1.5 e Å^{-3} near Au.

Full details of the structure determination (atom co-ordinates, complete bond lengths and angles, temperature factors, structure factors, libration correction) have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 53907. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

‡ The *X*-ray method was not able to distinguish between S and Cl in the presence of a gold atom. To resolve this problem, we attempted to prepare analogous Se or Br derivatives, but were unsuccessful. However, the chemical composition was unambiguously established, and other arrangements of S and Cl atoms are chemically less acceptable; in particular, an *S,Cl*-dithioformate ligand with an M–Cl–C structural unit and a non-co-ordinating S atom seems unlikely, especially at a relatively soft Au centre. A referee suggested the latter possibility and we stress that we cannot rule it out on crystallographic grounds alone.