The Crystal Structure of Carbonyl Gold(I) Chloride, (OC)AuCl

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The crystal structure of (OC)AuCl has been determined and refined to R 0.037 (space group $Cmcm$, $a = 407.1(1)$, $b = 1642.2(4)$, $c = 532.1(3)$ pm, $Z = 4$). The structure consists of discrete, exactly linear molecules; all atoms lie on the special positions 0, y, 1/4. The bond lengths involving the light atoms are affected by libration. The shortest Au···Au contacts between molecules are 338 pm.

Introduction

Carbonyl-gold(I)-chloride, (OC)AuCl, was first prepared in 1925 [1], as an extremely moisture-sensitive colourless crystalline solid, by the reaction of carbon monoxide with solid gold(III)-chloride. A more convenient method involves thionyl chloride as solvent [2], thus excluding moisture. The compound finds wide usage in preparative gold chemistry, since the carbonyl ligand is readily replaceable. A notable IR spectroscopic feature is the very high C–O stretching vibration frequency [2] (2152 to 2162 cm^{-1}, slightly solvent dependent), despite the low oxidation state d^{10} metal atom. This would imply little π back donation from the metal to the carbonyl group, as is confirmed by the Mössbauer spectrum [3].

Only one other gold carbonyl complex $Au_2(CO)Cl_4$, is known, and that only as a probable reaction intermediate [4, 5]. We have undertaken the crystal structure of (OC)AuCl as an attempt to provide more information about gold carbonyl complexes.

Data collection and structure solution

Colourless plates were obtained by crystallisation from thionyl chloride/petroleum ether and sealed in glass capillaries; thus protected from moisture, the crystals are stable for at least 2 years at —10 °C. A Stoe four-circle diffractometer (MoKα radiation, $\lambda = 71.069$ pm) was used to measure 3247 profile-fitted [6] intensities (a complete sphere collected twice) up to $2\theta_{\max}$ 55°. Systematic absences were hkl, $h+k$ odd and $h0l$, l odd, consistent in the orthorhombic system with space group $Cmcm$ or $Cmc2_1$. Cell constants were obtained from 2θ values of 30 strong reflections in the range $20° < 2\theta < 25°$.

Despite the small size of the crystal ($0.19 \times 0.15 \times 0.03$ mm) absorption effects were severe. After Lp corrections, an empirical absorption correction based on indexed faces ± 010 (plate faces), 101, $10\overline{1}$ (bounding faces), was applied. Averaging equivalents then gave 255 unique reflections, 252 of which with $F > 4\sigma(F)$ were classed as observed. A further five reflections very severely affected by absorption (mostly $0k0$ reflections) were later omitted.

The structure was solved by the heavy atom method and refined in space group $Cmcm$ with Au and Cl anisotropic, C and O isotropic. The final R was 0.037, with R_w 0.038 (weighting scheme $w^{-1} = \sigma^2(F) + 0.0005\,F^2$)). An extinction correction (whereby F was multiplied by $(1-7.9 \times 10^{-7} F^2/\sin\theta)$) was applied. Final atomic coordinates and related parameters are given in the Table. A final difference map showed one peak of 2.5 e Å^{-3} near the gold atom, otherwise no peak > 1 e Å^{-3}. An attempt at refinement with C and O exchanged increased R and R_w by 0.3%.

Crystal data

AuCClO, M = 260.43. Orthorhombic, space group $Cmcm$, $a = 407.1(1)$, $b = 1642.2(4)$, $c = 532.1(3)$ pm, U = 0.3557 nm^3, $Z = 4$, $D_x = 4.86$ Mg m^{-3}.

Discussion

All atoms lie on special positions 0, y, 1/4 with site symmetry mm; the molecules are thus exactly linear. The Au–C bond is short (193(2) pm), the only shorter example being 185(4) pm in Ph_3PAuCN [7], and the C–O bond is also short (111(3) pm). These short bonds may be ascribed to the effects of libration, no correction for which can be applied in the absence of reliable anisotropic thermal parameters for the

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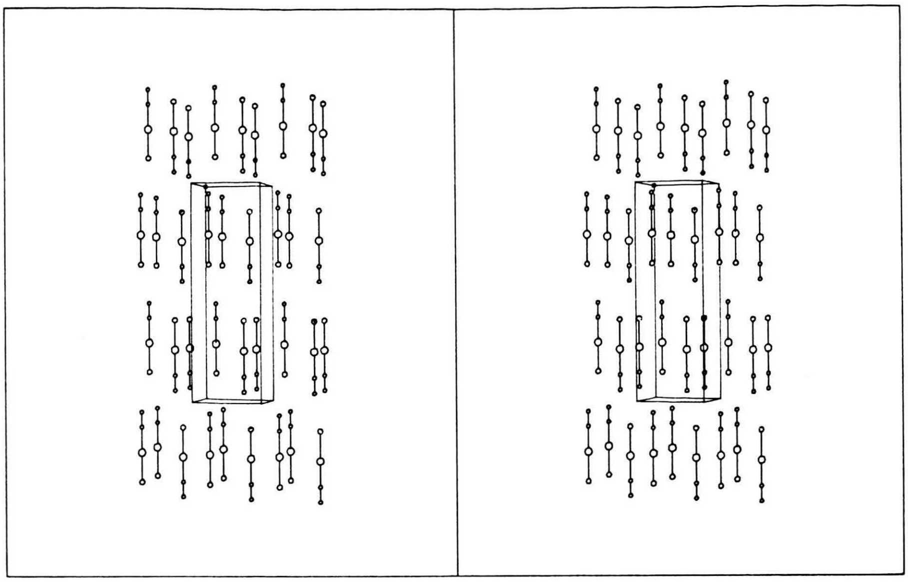

Fig. 1. Stereo plot of the packing of (OC)AuCl molecules.

Tab. I. Atom coordinates ($\times 10^4$), thermal parameters ($pm^2 \times 10^{-1}$) and bond lengths (pm).

Atom*	y	U_{11}	U_{22}	U_{33}
Au	2363(1)	62(1)	51(1)	43(1)
Cl	3739(4)	73(3)	53(3)	66(3)
C	1190(14)	51(4)		
O	515(13)	74(4)		

* All atoms lie at $x = 0$, $z = 0.25$. Au and Cl have $U_{23} = U_{13} = U_{12} = 0$ (symmetry restricted).

Au–Cl	226.1(6)
Au–C	193(2)
C–O	111(3)

All bond angles are (by symmetry) exactly 180 °C.

light atoms; an attempt to perform such corrections after anisotropic refinement of C and O proved unsuccessful, presumably because the thermal parameters cannot be reliable for light atoms in a highly absorbing material. Other physical methods will be necessary to obtain more reliable bond lengths.

Many gold(I) compounds are characterised by short (*ca.* 300 pm) intermolecular contacts between gold atoms; a review of such compounds has recently been published [8]. It has been suggested that the ease of packing of linearly coordinated complexes, rather than any weak bonding interaction, leads to these contacts. The packing of (OC)AuCl (Fig. 1) is such that the shortest Au ··· Au distances are 338 pm (to Au at $\pm 1/2$, $1/2 - y$, $1/4 \pm 1/2$). The gold atoms thereby achieve a pseudo-octahedral coordination.

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