Synthesis and Molecular Structure of $[Au_4Cl_8]$,† and the Isolation of $[Pt(CO)Cl_5]^-$ in Thionyl Chloride

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A high-yield synthesis of $[Au_4Cl_8]$ by treatment of $[Au_2Cl_6]$ with the stoicheiometric amount of CO in $COCl_2$ is described. The crystal and molecular structure of the tetranuclear compound has been solved by *X*-ray diffraction methods. It is triclinic, space group $P\bar{1}$, with a = 7.015(4), b = 6.830(2), c = 6.684(4) Å, α = 94.4(1), β = 107.5(1), γ = 88.4(1)°, and Z = 1, and has been refined to R = 0.11 for 989 ' observed ' reflections. The structure consists of discrete $[Au_4Cl_8]$ molecules with square-planar gold(III) and almost linear gold(I) centres in a chair-like arrangement. The solid compound has a high reactivity towards CO. The platinum(IV) derivative $[Pt(CO)Cl_5]^-$ has been isolated in $SOCl_2$ from the reaction of $[Pt(CO)Cl_3]^-$ with chlorine.

Earlier work from these Laboratories has shown that halogenocarbonyl complexes of late transition elements can be obtained by carbonylation of halogeno-complexes of gold,[1] palladium,[2] and platinum.[3] On the way from $[Au_2Cl_6]$ to [Au(CO)Cl] a mixed-valence compound of composition $[Au_4Cl_8]$ was isolated.[4] A preliminary account of the crystal and molecular structure of $[Au_4Cl_8]$ has appeared.[5]

We now report the one-step synthesis of $[Au_4Cl_8]$, the full details of its structural investigation, and the isolation, in $SOCl_2$ as solvent, of the product resulting from the known [6] reaction of dichlorine with $[Pt(CO)Cl_3]^-$.

Experimental

Thionyl chloride (C. Erba) was used without further purification. Other solvents were dried by conventional methods prior to use. Unless otherwise stated, all the operations were carried out under an atmosphere of purified nitrogen. Anhydrous gold(III) chloride was prepared from commercially available tetrachloroauric acid as previously described.[1] I.r. spectra were measured with a Perkin-Elmer model 283 instrument equipped with grating and CaF_2 cells. Experiments carried out in KBr cells sometimes gave erratic results due to reaction of the solution with the window material.

Preparation of $[Au_4Cl_8]$.—Anhydrous gold(III) chloride (3.07 g, 10.12 mmol of gold) was suspended in thionyl chloride (50 cm³) in a flask of known volume. The flask was evacuated and then filled with carbon monoxide (5.06 mmol) at atmospheric pressure. The contents of the flask were then stirred at 20.1 °C until the red $[Au_2Cl_6]$ had disappeared and was substituted by the black microcrystalline $[Au_4Cl_8]$, which usually required 36 h. The product was filtered off under nitrogen and dried *in vacuo* (67% yield). The mother-liquor was shown to contain $COCl_2$ [ν(CO) at 1 804 cm⁻¹]. The compound had the properties reported for the product obtained as described earlier [4] from the reaction of anhydrous $AuCl_3$ with [Au(CO)Cl].

The reaction of solid $[Au_4Cl_8]$ with excess of CO was monitored gas volumetrically: at 24.2 °C, 2 mol of CO were absorbed per mol of tetramer. The i.r. spectrum of the resulting yellow solid dissolved in thionyl chloride showed the band at 2 180 cm⁻¹ typical [4] of $[Au_2(CO)Cl_4]$, in addition to one at 2 162 cm⁻¹ due to [Au(CO)Cl]. The reaction of $[Au_4Cl_8]$ with the stoicheiometric amount of carbon monoxide required to form $[Au_2(CO)Cl_4]$ (2 mol of CO per mol of tetramer) did not give the dimer only, as evidenced by bands at 2 162 and 1 804 cm⁻¹, due to [Au(CO)Cl] and $COCl_2$, respectively. At the same time, precipitation of some $[Au_4Cl_8]$ was noted.

X-Ray Data Collection for $[Au_4Cl_8]$ *and Solution and Refinement of Structure*.—Crystals were grown by letting a suspension of $[Au_2Cl_6]$ in thionyl chloride react with a diluted solution of [Au(CO)Cl] in the same solvent under diffusion-controlled conditions. Several needle-shaped crystals were closed in Lindemann capillaries, carefully avoiding contact with air. All of them, examined by Weissenberg and precession methods, showed similar diffraction patterns. The Weissenberg spectra, for instance, were recorded with c as oscillating axis, which in our case coincided with the elongation axis of the crystals. While the $hk0$ plane gave a spectrum compatible with that of a triclinic crystal, the $hk1$ and $hk2$ planes, in addition to their triclinic symmetry, showed double spots, with the same θ values but different ω values. The intensity of one of the two spots of a given couple was regularly lower than that of the other. For each individual couple the difference in ω value was constant for l constant and increased with l. This behaviour has been interpreted as being due to twinning, where one of the two lattices is generated from the other by a 180° rotation around the [001] axis, and confirmed by the subsequent solution of the structure.

The crystal with the best diffraction pattern had dimensions 0.9 × 0.06 × 0.015 mm and the intensity data were measured with an automated Siemens AED diffractometer with Zr-filtered Mo-K_α radiation. The θ–2θ scan method and the ' five-points ' technique [7] were used.

Crystal data. Au_4Cl_8, M = 1 071.5, Triclinic, space group $P\bar{1}$, a = 7.015(4), b = 6.830(2), c = 6.684(4) Å, α = 94.4(1)°, β = 107.5(1), γ = 88.4(1)°, U = 304.5 Å³, Z = 1, D_c = 5.84 g cm³, $F(000)$ = 452, μ(Mo-K_α) = 511 cm⁻¹, λ(Mo-K_α) = 0.710 69 Å.

1 466 Reflections were collected and 989 of them with $I \geqslant 3.0\sigma(I)$, where $\sigma^2(I)$ = total counts + $(0.005\ I)^2$, were used for the structure determination. Intensity fluctuations were monitored by a standard reflection, measured every 15 reflections; the maximum long-term variation was about 4%. An absorption correction was applied using the method of Busing and Levy,[8] assuming a somewhat idealized shape. The transmission-factor range was 0.092—0.467.

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† 1,2;1,4;2,3;3,4-Tetra-μ-chloro-1,1,3,3-tetrachloro-*cyclo*-tetragold.

Supplementary data available (No. SUP 23383, 12 pp.): thermal parameters, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Fractional atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for $[Au_4Cl_8]$

Atom	X/a	Y/b	Z/c
Au(1)	0.470 9(3)	0.507 9(3)	0.261 9(3)
Au(2)	0.095 4(3)	0.236 0(3)	0.381 1(3)
Cl(1)	0.301(2)	0.218(2)	0.164(2)
Cl(2)	0.372(2)	0.192(2)	0.668(2)
Cl(3)	−0.104(2)	0.256(2)	0.588(2)
Cl(4)	−0.177(2)	0.272(2)	0.101(2)

The molecular structure was solved by Patterson and Fourier methods and refined by least-squares methods with anisotropic thermal parameters for all of the atoms. Two scale groups were used for the observed structure factors: one for the *hk*0 reflections and another for the *hkl* reflections with $l \neq 0$. The scale factors at the end of refinement were 2.07 and 2.14, respectively. The final R value was 0.11 [$R' = 0.15$ where $w = 1/(1 + F_0 + 0.02F_0^2)$], which is considered acceptable taking into account both the twinning and the poor quality of the crystal. Table 1 gives the final positional atomic parameters.

Preparation of $[NH_2Pr^i_2][Pt(CO)Cl_5]$.—A thionyl chloride (5 cm^3) solution of $[Pt(CO)Cl_3]^-$ was obtained by treating $[Pt(CO)_2Cl_2]$ (0.55 g, 1.70 mmol) with $NH_2Pr^i_2Cl$ for 30 h at about 60 °C under an atmosphere of prepurified nitrogen.

The anion is characterized by an i.r. absorption at 2 116 cm^{-1} in concentrated HCl and at 2 107 cm^{-1} in dichloromethane. Addition of dichlorine (1.1 g, 15.5 mmol) at room temperature resulted in the prompt formation of the carbonyl-stretching vibration at 2 191 cm^{-1} due to the new product. The reaction was over in a few minutes. The yellow-orange product was precipitated with CCl_4, filtered off, and dried *in vacuo* (72% yield) (Found: CO, 5.45; Pt, 40.3. Calc. for $C_7H_{16}Cl_5NOPt$: CO, 5.7; Pt, 39.6%). The compound is stable towards Cl^- in both $CCl_4 + SOCl_2$ and *sym*-$C_2H_2Cl_4$ under carbon monoxide, since no displacement of co-ordinated carbon monoxide was observed at room temperature by treatment with $NH_2Pr^i_2Cl$, as monitored by i.r. spectroscopy and gas-volumetric measurements. On the other hand, the compound reacts promptly with water evolving carbon dioxide quantitatively according to the stoicheiometry (1).

$$[Pt(CO)Cl_5]^- + H_2O \longrightarrow CO_2 + [PtCl_4]^{2-} + HCl + H^+ \tag{1}$$

This reaction was used analytically for the determination of the CO content. The presence of Pt^{II} in solution was demonstrated by precipitation of the 2,2′-bipyridyl adduct $[PtCl_2(bipy)]$, having an i.r. spectrum identical to that of an authentic sample.[9]

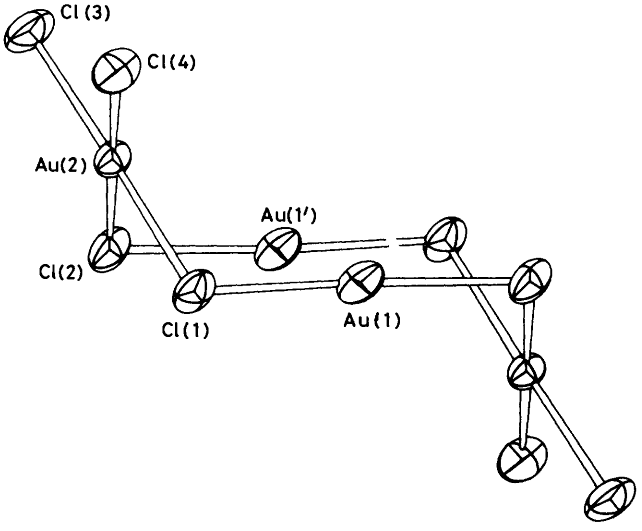


Figure 1. ORTEP view of $[Au_4Cl_8]$ molecules, with the numbering scheme used

Results and Discussion

Previous work on the mixed-valence compound $[Au_4Cl_8]$ had shown[4] that the appropriate stoicheiometry for the preparation of the compound was as in equation (2). Having observed that

$$3AuCl_3 + [Au(CO)Cl] \longrightarrow COCl_2 + [Au_4Cl_8] \tag{2}$$

the bonded carbon monoxide in this system never leaves the co-ordination sphere as such but rather is transformed into the thermodynamically more stable $COCl_2$ [$CO + Cl_2 \longrightarrow COCl_2$, $\Delta H = -109.2$ kJ mol^{-1} (ref. 10)], we successfully attempted the one-step preparation of the mixed-valence gold(I)-gold(III) compound directly from anhydrous gold(III) chloride and CO by using the correct amount of CO in thionyl chloride as solvent [equation (3)]. The use of larger or smaller

$$4AuCl_3 + 2CO \longrightarrow [Au_4Cl_8] + 2COCl_2 \tag{3}$$

quantities of CO led to the formation of $[Au_4Cl_8]$ contaminated by $[Au_2(CO)Cl_4]$[4] and [Au(CO)Cl] or by $AuCl_3$, respectively. It should be noted that this method does not require the use of pre-isolated $[Au_2Cl_6]$, since the latter can be discontinuously prepared *in situ* by letting tetrachloroauric acid react with thionyl chloride under an inert atmosphere, prior to reaction with CO.

The molecular structure (see Figures 1 and 2, Table 2) of the product obtained by reaction (3) consists of discrete $[Au_4Cl_8]$ molecules, with gold(III) and gold(I) centres, in idealized square-planar and linear geometries, respectively (see below). It has several interesting features. First, most of the known mixed-valence compounds of gold are multicentric systems loosely joined by halide bridges: these systems can be either ionic or uncharged. Known examples are: $Cs_2Au_2Cl_6$ discovered by Wells[11] and subsequently studied crystallographically,[11-13] $Rb_2Au_2Br_6$ and $Rb_3Au_3Cl_8$,[14] $Rb_2AgAu_3I_8$,[15] and the benzyl sulphide complex $[AuBr_2(SCH_2C_6H_5)_2]$.[16]

In the present case, the gold(I) and gold(III) centres are joined by chloride bridges in a covalently bonded molecular structure. The gold(III)-terminal chloride bond distance is 2.25 Å (average) which is consistent with the similar distance found in $[Au_2Cl_6]$[17] (2.24 Å, average). On the other hand, the bridging chloride between the gold(III) and the gold(I) centres in $[Au_4Cl_8]$ is at 2.32(2) Å from gold(III) and at 2.30(1) Å from gold(I). While the former value is in agreement with the corresponding bond distance for bridging chlorides in $[Au_2Cl_6]$ (2.33 Å), the latter is significantly shorter than the Au−Cl (2.36 Å) distance in the zigzag chain of AuCl.[18] The Au−Cl distances found for compounds containing the $[AuCl_2]^-$ ion are 2.27(4),[14] 2.31,[12] and 2.293(15) and 2.260(14),[19,20] which are approximately the same, within experimental error, as our value.

As already mentioned, the co-ordination geometry around the central gold(I) centre is almost linear. However, a significant distortion from linearity is clearly indicated by the Cl(1)−Au(1)−Cl(2′) angle being 175.1(5)°. The deviation from

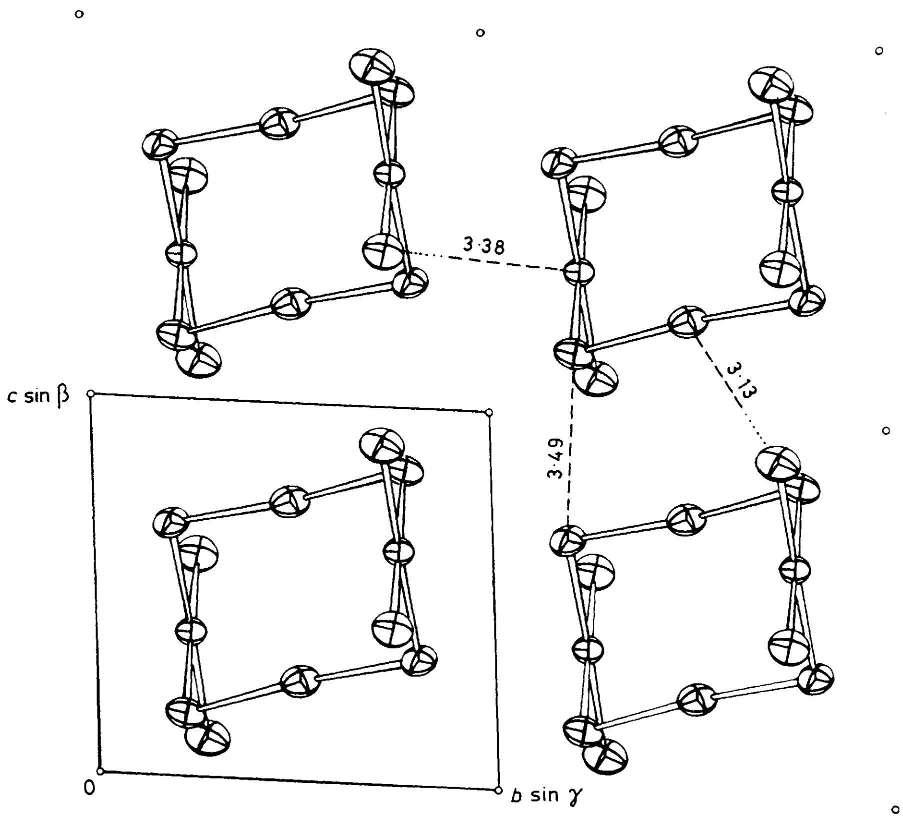


Figure 2. An ORTEP representation of crystal packing of $[Au_4Cl_8]$ projected along the *a* axis (50% probability ellipsoids). Some intermolecular distances are indicated

Table 2. Bond distances (Å) and angles (°) for $[Au_4Cl_8]$ with e.s.d.s in parentheses

Au(1)-Cl(1)	2.29(1)	Au(2)-Cl(2)	2.31(1)
Au(1')-Cl(2)	2.31(1)	Au(2)-Cl(3)	2.24(2)
Au(1)···Au(1')	3.095(4)	Au(2)-Cl(4)	2.26(1)
Au(2)-Cl(1)	2.33(2)		
Cl(1)-Au(1)-Cl(2')	175.1(5)	Cl(1)-Au(2)-Cl(3)	179(1)
Cl(1)-Au(1)-Au(1')	95.5(4)	Cl(2)-Au(2)-Cl(3)	90.8(5)
Cl(2')-Au(1)-Au(1')	89.0(4)	Cl(2)-Au(2)-Cl(4)	178.6(9)
Au(2)-Cl(1)-Au(1)	101.6(5)	Cl(3)-Au(2)-Cl(4)	88.8(6)
Au(2)-Cl(2)-Au(1')	104.3(5)	Cl(4)-Au(2)-Cl(1)	90.8(5)
Cl(1)-Au(2)-Cl(2)	89.6(5)		

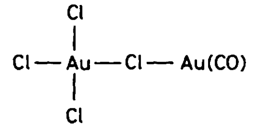
Primes indicate the equivalent position 1 − *x*, 1 − *y*, 1 − *z*.

linearity is such as to bring the two gold(I) atoms closer together, thus showing an attractive interaction between them. The Au(1)···Au(1') distance in 3.095(4) Å, to be compared with 2.884 Å found for the metal itself[21] and 2.83,[22] 2.98 (average),[23] 3.02 (average),[24] and 2.80—2.94[25] for peripheral Au–Au distances in some clusters. Several cases of short-range interactions between gold(I) atoms have been reported in the literature. In polymeric AuCl itself[18] there are gold–gold contacts of 3.37 Å. Au···Au contacts ranging from 2.70 to 3.40 Å are known for gold(I) complexes.[20,26] Our compound may be regarded as an eight-membered annular compound, containing alternate Au and Cl atoms in the ring. Attractive interactions are well known in annular gold(I) complexes containing heteroatoms such as sulphur and phosphorus.[20,27]

It is interesting to regard the central gold(I) atoms of $[Au_4Cl_8]$ as quasi T-shaped three-co-ordinate. The tendency of the gold(I) centres to expand their co-ordination sphere is also evidenced by the prompt reaction of solid $[Au_4Cl_8]$ with CO which gave [equation (4)] the gold(III)–gold(I) carbonyl adduct, $[Au_2(CO)Cl_4]$, suggested[4] to have structure

$$[Au_4Cl_8] + 2CO \longrightarrow 2[Au_2(CO)Cl_4] \qquad (4)$$

(I). In thionyl chloride as solvent with the stoicheiometric amount of CO required for equation (4), the reaction was more complicated and [Au(CO)Cl], $[Au_4Cl_8]$, and $COCl_2$ were observed as products, besides $[Au_2(CO)Cl_4]$. This can be explained by assuming that $[Au_2(CO)Cl_4]$ is in equilibrium with [Au(CO)Cl] and $[Au_2Cl_6]$, the latter being sufficiently soluble in thionyl chloride (about 5 g l^{-1}) to sustain the equilibrium. Over long reaction times, $[Au_4Cl_8]$ and $COCl_2$ were observed, due to further reaction of $[Au_2Cl_6]$ with [Au(CO)Cl], as shown earlier.[4]



$$Cl-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{Au}}-Cl-Au(CO)$$

(I)

It is easy to see that conversion of $[Au_4Cl_8]$ into $[Au_2(CO)Cl_4]$ requires breaking of the chloride-bridged central part of the tetramer, presumably as a consequence of preliminary co-ordination of carbon monoxide to gold(I). While two-co-ordinate gold(I) occurs frequently, there are also examples in the literature of three-[20] and four-co-ordinate[28] gold(I).

The square around the gold(III) atoms is practically planar, the maximum deviation from planarity being 0.02 Å. The

Table 3. Some intermolecular distances (Å) for [Au_4Cl_8]

$Au(1)\cdots Cl(4^{I})$	3.13	$Cl(1)\cdots Cl(2^{V})$	3.49
$Au(1)\cdots Cl(4^{II})$	3.31	$Cl(1)\cdots Cl(2^{VI})$	3.60
$Au(1)\cdots Cl(3^{III})$	3.36	$Cl(3)\cdots Cl(4^{VII})$	3.61
$Au(2)\cdots Cl(3^{IV})$	3.38	$Cl(2)\cdots Cl(4^{VIII})$	3.61

Symmetry-equivalent positions: I $-x, 1-y, -z$; II $1+x, y, z$; III $-x, 1-y, 1-z$; IV $-x, -y, 1-z$; V $x, y, z-1$; VI $1-x, -y, 1-z$; VII $x, y, 1+z$; VIII $1+x, y, 1+z$.

Au(1), Au(1′), Cl(1), Cl(1′), Cl(2), Cl(2′) system is also substantially planar, the maximum deviation being 0.03 Å. The dihedral angle between these two planes is 69°.

It is interesting to postulate a possible explanation for the black colour of [Au_4Cl_8], which is certainly associated with the mixed-valence nature of this compound. As indicated in Table 3, significant $Au\cdots Cl$ contacts range from 3.13 to 3.38 Å, the former being that between a gold(I) atom of one molecule and a terminal chloride of the next molecule. This approach is rather long with respect, for example, to the $Au\cdots Cl$ non-bonding distance (2.9 Å) in $Cs_2Au_2Cl_6$.[11,12] The closest intermolecular $Au^{I}\cdots Au^{III}$ approach in our compound is higher than 4.4 Å, while there is an intramolecular $Au^{I}\cdots Au^{III}$ approach of 3.58(1) Å. For these reasons, it is reasonable to assume that an electron experiences intramolecular transfer between the gold(I) and the gold(III) centres either through the chloride bridges or through space.

Finally, mention should be made of the fact that this study definitely establishes the existence of a compound of empirical formula $AuCl_2$, contrary to the conclusions [29] recently drawn on the basis of the thermal analysis of the gold–chlorine system. Of course, our compound can only be obtained at room temperature by the method outlined, namely by co-ordinated carbonyl reduction of gold(III), since it is metastable with respect to $AuCl_3$ and AuCl at 260 °C.[29]

Both [Au(CO)Cl] and the 1 : 1 adduct [$Au_2(CO)Cl_4$] are characterized by very high ν(CO) for the co-ordinated carbonyl group, 2 162 and 2 180 cm^{-1}, respectively, in thionyl chloride as solvent.[1,4] These high values suggest a very low, if any, degree of π-back donation from the metal to carbon monoxide.[30]

In agreement with the recently reported [6] oxidation of $[Pt(CO)Cl_3]^-$ by dichlorine, we have succeeded in isolating the $[Pt(CO)Cl_5]^-$ anion as the di-isopropylammonium derivative, using thionyl chloride as solvent. This anion is characterized by a CO stretching vibration in this solvent at 2 191 cm^{-1}, which we believe to be the highest ever recorded for a carbonyl derivative of a transition element.

By using thionyl chloride as solvent, which is unreactive towards dichlorine, rather than dichloromethane,[6] it was possible to obtain sufficiently stable solutions of the $[Pt(CO)Cl_5]^-$ anion. Despite the presumably particularly weak Pt–CO bond of this compound, its conversion into reduced products is rather slow, in agreement with the usually low kinetic lability of d^6 platinum(IV) complexes. However, a prompt reaction with water was observed, carbon dioxide being readily evolved, presumably by OH^- attack at the co-ordinated carbonyl group.

Acknowledgements

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