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The Crystal Structure of Gold (III) Chloride*

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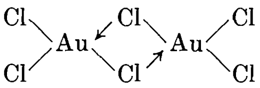
Gold (III) chloride is monoclinic, in space group $P2_1/c$, with cell dimensions $a = 6{\cdot}57$, $b = 11{\cdot}04$, $c = 6{\cdot}44$ Å, and $\beta = 113{\cdot}3°$. The atomic positions were determined by Patterson and electron-density projections and were refined by Fourier and least-squares methods with three-dimensional data. The structure consists of planar molecules Au_2Cl_6 (at centers of symmetry) in which each Au has four Cl neighbors at 2·23 and 2·25 Å (terminal Cl) and 2·33 and 2·34 Å (bridge Cl), each ±0·02 Å. Gold scattering factors in the least-squares refinement were modified for dispersion with little effect on coordinates but with appreciable effect on temperature and scale factors.

Introduction

Gold (III) chloride sublimes readily at elevated temperatures. Gas density measurements by Fischer (1929) show that it occurs in the vapor as Au_2Cl_6 molecules. No study of the molecular structure seems to have been reported, but Wells (1947), by analogy to the square planar bonding of gold (III) in other compounds, has predicted the planar structure



The present investigation by X-ray diffraction of the structure of the crystals demonstrates that discrete dimer molecules persist in the solid and confirms the molecular structure predicted by Wells.

Preparation and morphology

Freshly snipped gold foil was placed in a glass tube in a furnace. After chlorine had been introduced into a side-arm and frozen with liquid nitrogen, the system was evacuated with mercury diffusion pumps and sealed. The pressure of the chlorine was raised to about four atmospheres by replacing the nitrogen bath with ice water. The gold metal was then heated, and crystals of gold chloride grew by sublimation at the cool ends of the furnace. When a suitable quantity of crystals had been collected, the nitrogen bath was again placed about the chlorine and the portion of the system containing the crystals was sealed off. The tube containing the very hygroscopic gold chloride crystals was subsequently broken open inside a dry-box. Crystals of suitable size and morphology were selected and sealed in very thin-walled glass capillary tubes for X-ray photography.

A method for the preparation of single crystals of gold chloride from the hydrate was devised and executed by Mr A. Kreuger of the Netherlands Organization for Pure Research (Z. W. O.). Gold chloride hydrate was dried under vacuum at room temperature for 24 hr. The temperature was then raised above 100° C. and the evolved water was distilled into a side-arm immersed in a liquid-air bath. Following removal of water, the remaining crystalline material was kept at slightly above 100° C. for several days. Minute crystals of gold chloride were observed growing slowly by sublimation in a cool part of the system. When the desired number of crystals had been prepared, heating was discontinued. Under a positive pressure of very dry nitrogen, some of the tiny crystals were coaxed into thin-walled glass capillary tubes attached to the system and these tubes containing the crystals were sealed off for mounting on a goniometer.

At 200° C., growth by sublimation was slow, with the formation of thin 'cellophane-like' crystals parallel to (100). At 280° C., growth was more rapid with the formation of [001] needles. A preparation which remained at 200° C. for 24 hr. and was then raised to 250° C. for several hours consisted of a lacy network of needles within thin plates. The needle preparations would sometimes appear fibrous when broken with a probe. The thin plates are orange; the needles are wine red. This is probably due to differences in light absorption with crystals of different thicknesses since X-ray diffraction patterns of needles and plates were identical.

Gravimetric analysis of the trichloride by decomposition with heat followed by absorption of the

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chlorine gave 35·20% chlorine against a theoretical 35·04%. We wish to thank Mr V. H. Tashinian of the microanalytical laboratory of the University of California for analyses of the chlorides.

Diffraction data

Weissenberg photographs, calibrated with quartz, and precession photographs corresponded to a monoclinic lattice (Cu $K\alpha = 1{\cdot}5418$ Å):

$$\text{Space group } P2_1/c;$$
$$a = 6{\cdot}57,\ b = 11{\cdot}04,\ c = 6{\cdot}44\ \text{Å},\ \beta = 113{\cdot}3^\circ.$$

Difficulties due to asymmetric shape and high absorption make these dimensions uncertain by perhaps 0·5%. With 4($AuCl_3$) per unit cell the density calculated is 4·70 g.cm.$^{-3}$ compared with 4·67 g.cm.$^{-3}$ measured by Fischer & Biltz (1928).

The final structure is based on data from a needle of dimensions $0{\cdot}072 \times 0{\cdot}11 \times 2{\cdot}2$ mm., rotated about [001]. Multiple-film Weissenberg layers 0–3 were taken with Cu radiation and their intensities were observed visually by comparison with standard spots. Layers 4–7 were photographed with Mo radiation and measured with a photometer. Careful attention was given to the sizes of the spots, which differed systematically from one side of the film to the other (Clark, 1955). The intensities within each layer were corrected for absorption on the assumption that the crystal was cylindrical, according to Bradley (1935), using $\mu r = 4{\cdot}3$ for Cu radiation and $\mu r = 2{\cdot}0$ for Mo radiation. The absorption due to the glass capillary should be constant within a layer, to a first approximation, because the capillary is nearly cylindrically symmetrical and is nearly coaxial with the camera. Because of severe difficulties due to absorption for crystals photographed in other geometries, the procedure finally adopted was to normalize one layer to the next on the basis of calculated intensities.

Data for some of the preliminary calculations were obtained from a Weissenberg ($hk\bar{h}$) photograph (rotation about [101]), which was corrected for absorption by a laborious procedure (Clark, 1955), and from a precession ($0kl$) photograph.

Determination of the structure

The probable space group $P2_1/c$ has general positions:

$$4(e):\ \pm(x, y, z;\ x, \tfrac{1}{2}-y, \tfrac{1}{2}+z)\ .$$

There are also twofold special positions without variable parameters. The gold atoms must be in one set of general positions because otherwise there would be systematic weak intensities corresponding to additional pseudo translation operations in the gold lattice.

A Patterson projection along [001] was readily interpreted to give approximate values of x and y for gold. The corresponding electron-density projection, with signs determined by gold alone, immediately showed the chlorine atoms, in three sets of general positions. This projection, after the subsequent correction of the data for absorption and a check of signs, is shown in Fig. 1.

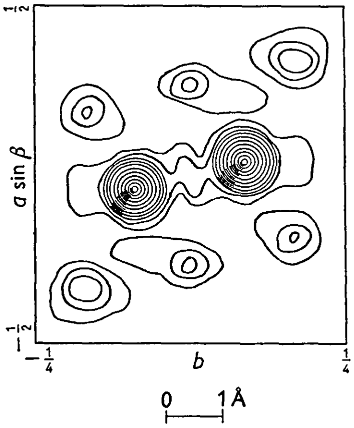


Fig. 1. Electron-density projection along [001]. Contours are at equal arbitrary intervals, with the zero contour omitted.

A Patterson projection with the ($0kl$) precession data revealed that z for gold was nearly 0·25. With this parameter, gold controls the signs of only half the reflections. The electron density calculated from these data shows the chlorine atoms doubled by a false mirror plane. The sign of one additional reflection is arbitrary at this point because of two possibilities of the location of the origin. Inclusion of (031), the only remaining strong reflection with arbitrary sign, revealed which chlorine peaks corresponded to one choice of origin. Refinement lead to a projection in which chlorine atoms Cl_{II} and Cl_{III} are resolved, but two peaks due to Cl_I are not resolved.

The projection along [101] was next refined. After subtraction of the contribution due to gold it showed all the chlorine atoms resolved, as in Fig. 2. Thus all the coordinates were determined approximately.

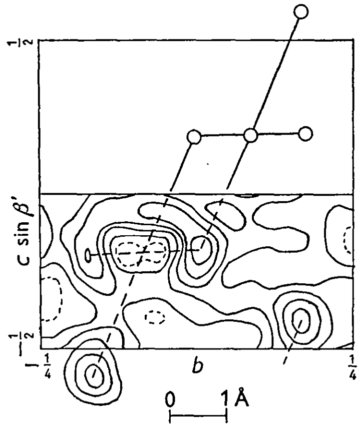


Fig. 2. Synthesis of $F_o - F_{Au}$, projected along [101]. Contours are at equal arbitrary intervals.

Table 1. *Observed and calculated structure factors*

The left-hand column is the value of k, the middle column is the magnitude of the real part of the observed structure factor, derived as explained in the text, and the right-hand column is the calculated real part of the structure factor.

	$0k0$	
0	—	125
2	34	32
4	39	−31
6	26	−21
8	12	−9
10	14	12
12	20	15
14	2	2

	$1k0$	
0	59	64
1	14	−9
2	33	29
3	18	−14
4	28	−30
5	8	−6
6	39	−38
7	5	4
8	11	−8
9	8	6
10	12	11
11	0	0
12	14	10
13	3	−2
14	2	2

	$2k0$	
0	35	26
1	0	1
2	19	17
3	25	−25
4	25	−26
5	17	−17
6	32	−41
7	15	15
8	10	−9
9	10	10
10	10	8
11	0	0
12	8	6
13	2	−2

	$3k0$	
0	42	34
1	22	−18
2	16	15
3	23	−28
4	12	−13
5	6	−8
6	16	−19
7	9	11
8	6	−5
9	12	12
10	8	7
11	3	3
12	8	6
13	4	−3

	$4k0$	
0	23	20
1	26	−24
2	18	15
3	26	−27
4	0	−3
5	3	−3
6	7	−10
7	4	7
8	0	0
9	12	11
10	6	6
11	4	4
12	4	4

	$5k0$	
0	7	7
1	12	−12
2	0	2
3	21	−23
4	4	−5
5	6	−8
6	5	−4
7	9	9
8	0	−1
9	11	9

	$6k0$	
0	0	2
1	9	−8
2	5	−4
3	16	−16
4	3	−4
5	6	−6
6	0	1
7	7	7
8	3	−2
9	6	8

	$7k0$	
0	3	−3
1	5	−6
2	0	0
3	9	−10
4	2	2
5	3	−4
6	1	2

	$0k1$	
1	14	6
2	54	−63
3	32	30
4	43	−38
5	4	−3
6	7	5
7	4	−2
8	26	23
9	10	8
10	17	14
11	0	2
12	3	−3
13	4	1
14	12	−7

	$0k2$	
0	41	−34
1	0	2
2	29	−23
3	13	−10
4	27	27
5	10	−9
6	44	43
7	8	6
8	10	8
9	5	4
10	14	−10
11	0	−1
12	10	−7
13	2	−1

	$0k3$	
1	12	−10
2	33	32
3	9	8
4	30	31
5	9	9
6	4	−3
7	7	7
8	20	−21
9	0	1
10	12	−9
11	5	−3
12	3	2

	$0k4$	
0	25	34
1	8	8
2	16	14
3	14	13
4	17	−15
5	5	3
6	24	−21
7	7	−5
8	8	−6
9	9	−6
10	10	8
11	0	−2
12	11	7
13	0	2

	$0k5$	
1	9	10
2	18	−18
3	0	−2
4	20	−17
5	12	−10
6	0	2
7	7	−6
8	13	11
9	0	1
10	7	5

	$0k6$	
0	13	−16
1	7	−7
2	9	−8
3	10	−10
4	7	6
5	0	−2
6	12	10
7	3	3
8	3	2
9	5	4
10	5	−4
11	0	1
12	6	−3
13	0	−2

	$0k7$	
1	7	−9
2	9	9
3	0	0
4	6	5
5	5	4
6	0	−1
7	4	3
8	5	−4
9	0	−1
10	4	−3
11	4	−3

	$1k\bar{1}$	
1	30	21
2	54	56
3	12	7
4	38	34
5	18	−12
6	5	−4
7	12	−9
8	25	−23
9	4	4
10	16	−14
11	7	6
12	3	3
13	0	2

	$2k\bar{2}$	
0	56	−50
1	37	33
2	32	−26
3	35	32
4	15	12
5	0	2
6	23	20
7	9	−7
8	5	4
9	13	−13
10	11	−10
11	4	−4
12	10	−8
13	5	4

	$3k\bar{3}$	
1	34	−42
2	24	−23
3	4	4
4	10	−8
5	18	18
6	0	2
7	12	12
8	8	6
9	3	−2
10	8	6
11	12	−11

	$4k\bar{4}$	
0	0	2
1	13	−16
2	5	4
3	26	−28
4	0	0
5	11	−10
6	0	−3
7	14	11
8	0	0
9	15	14

	$5k\bar{5}$	
1	17	24
2	9	−8
3	0	−2
4	0	−1
5	12	−12
6	0	0
7	10	−7
8	0	1
9	0	2
10	0	2
11	8	7

	$6k\bar{6}$	
0	7	9
1	6	7
2	4	4
3	9	11
4	1	−3
5	4	3
6	6	−5
7	4	−4
8	0	−1
9	7	−5
10	5	2

	$7k\bar{7}$	
1	4	−5
2	5	7
3	0	−1
4	5	4
5	3	3
6	0	−1
7	3	2
8	4	−4

Because of dissatisfaction with the accuracy of these projections, we collected the three-dimensional data. Plane sections were calculated through each atom parallel to (010). Then, at each maximum, line sections were calculated parallel to b. The results of these calculations, with no correction for series termination, are:

	x	y	z
Au	0·0414	0·0868	0·2336
$\mathrm{Cl_I}$	0·254	0·006	0·060
$\mathrm{Cl_{II}}$	0·334	0·170	0·508
$\mathrm{Cl_{III}}$	0·819	0·162	0·385

Least-squares refinement

At this point we gained access to an International Business Machines type 650 data-processing machine. A program for refinement by the method of least squares had been prepared for this machine mostly by Dr Michael E. Senko. Each atom was assigned an individual isotropic temperature factor, $\exp(-B\sin^2\theta/\lambda^2)$. Because of the normalization procedure, these temperature factors refer essentially to the amplitudes of vibration in the xy plane. The scattering factors for chlorine were taken from Berghuis *et al.* (1955). The scattering factors for gold (*International Tables*, 1935) were modified to take account of dispersion (Dauben & Templeton, 1955):

$$f = f_0 - 5 + 8i \quad \text{for Cu } K\,,$$
$$f = f_0 - 2{\cdot}4 + 9{\cdot}8i \text{ for Mo } K\,.$$

The least-squares procedure was modified so that A_c the real part of F_c, was fitted to $F_oA_c/\sqrt{(A_c^2+B_c^2)}$, which is our best estimate of the real part of the observed structure factor; B_c is the imaginary part of F_c. In this problem the dispersion effects are not extreme. For about 800 observed reflections the correction factor on F_o was less than 0·95 for only 30 reflections and never less than 0·85. The zero-layer data were refined both with and without dispersion, to test its effect, and the resulting coordinates agreed within 0·001 for Cl and 0·0001 for Au. On the other hand, temperature factors differed by 5–8% and normalization factors by 7% because of the different angular dependence of the scattering factors, as predicted elsewhere (Templeton, 1955). The data were weighted in the least squares according to $1/F_o^2$ or 1/100, whichever was smaller.

The final coordinates and temperature factors derived by this method from the three-dimensional data, including about 250 unobserved reflections, are:

	x	y	z	$B \times 10^{16}$ (cm.^{2})
Au	0·0415	0·0868	0·2337	3·3
Cl_I	0·258	0·003	0·059	4·1
Cl_II	0·335	0·169	0·509	4·8
Cl_III	0·820	0·162	0·395	4·9

The standard deviations in the coordinates calculated from the residuals in the least-squares method are:

	σ_x	σ_y	σ_z
Au	0·0002	0·0001	0·0003
Cl_I	0·002	0·001	0·002
Cl_II	0·002	0·001	0·003
Cl_III	0·002	0·001	0·003

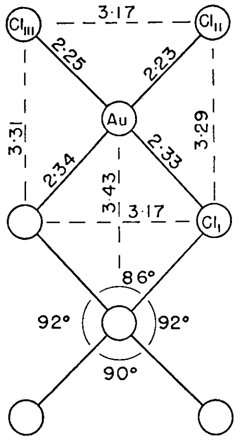


Fig. 3. Molecular dimensions of Au_2Cl_6. The molecule has a center of symmetry. The standard deviation of each bond length is about 0·02 Å, considering the uncertainties of both the coordinates and the cell dimensions.

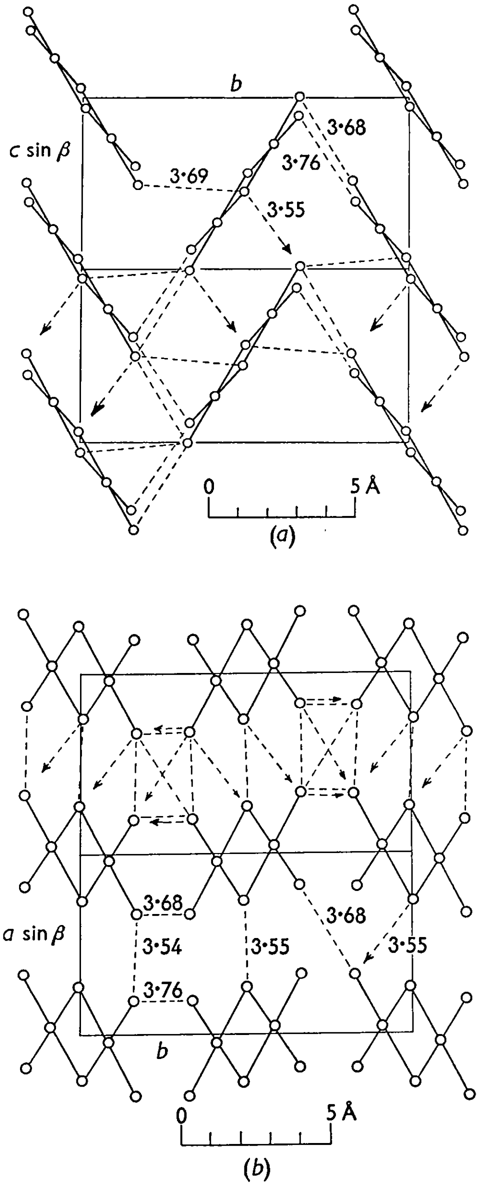


Fig. 4. (*a*) Structure of gold chloride projected along [100]. Short distances (in Å) of chlorine atoms in adjacent molecules are stated and indicated by dashed lines. The lines terminated by arrows lead to the corresponding atom in the next layer above. Two unit cells are indicated by the rectangles. (*b*) Structure of gold chloride projected along [001]. Two unit cells are indicated by the rectangles. Short Cl–Cl distances are indicated as in (*a*).

The conventional R index achieved 0·20, or 0·15 for observed reflections only. The 'weighted root-mean-square' reliability index:

$$R_2 = \sqrt{\left\{\frac{\Sigma w|F_o - F_c|^2}{\Sigma w|F_o|^2}\right\}}\,,$$

which is the quantity actually minimized by the least-squares method, achieved 0·25, including unobserved reflections. A portion of the data is tabulated in Table 1; complete data are given by Clark (1955).

Discussion of the structure

The crystal consists of discrete molecules Au_2Cl_6, each located about a center of symmetry. If a plane is passed through the center of symmetry and atoms Cl_{II} and Cl_{III}, then Au and Cl_I are both within 0·01 Å of this plane. Thus the molecule is planar within experimental error. The experimental bond lengths and angles are shown in Fig. 3.

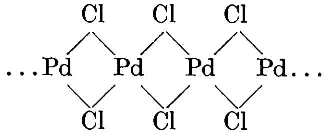
The molecules are packed together as shown in Fig. 4. This arrangement is closely related to those of naphthalene (Abrahams, Robertson & White, 1949) and related planar hydrocarbons. It differs in that the short dimension of the molecule, rather than the long dimension, is nearly parallel to *a*. The shortest distances between chlorine atoms in adjacent molecules are 3·54 Å.

The square planar bonding of tripositive gold is explained by Pauling (1942) on the basis of dsp^2 orbitals with the following electronic structure of gold:

$$(2)\ (8)\ (18)\ (32)\ \overset{5s}{(2)}\ \overset{5p}{(6)}\ \overset{5d}{(8+}\underbrace{2)\ \overset{6s}{(2)}\ \overset{6p}{(4)}}_{\text{Shared}}\ .$$

In accord with this configuration, auric chloride is diamagnetic (Klemm & Tilk, 1932). Several other compounds in which this square coordination has been observed are listed by Pauling (1942).

The deviations from right angles of the bridge bonds are analogous to the situation in $PdCl_2$ (Wells, 1938), where infinite chains exist:



The bridge bonds make an angle of 87° at the palladium atom, compared to the 86° angle in gold chloride. The deviations from 90° are presumably the result of repulsion by the metal atoms; for the terminal chlorine atoms, where no gold–gold repulsion operates, the bonds make a right angle.

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References

ABRAHAMS, S. C., ROBERTSON, J. M. & WHITE, J. G. (1949). *Acta Cryst.* **2**, 238.
BERGHUIS, J., HAANAPPEL, I. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
BRADLEY, A. J. (1935). *Proc. Phys. Soc.* **47**, 879.
CLARK, E. S. (1955). Ph.D. Dissertation, University of California, Berkeley.
DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.
FISCHER, W. (1929). *Z. anorg. Chem.* **184**, 333.
FISCHER, W. & BILTZ, W. (1928). *Z. anorg. Chem.* **176**, 81.
International Tables for the Determination of Crystal Structures, vol. 2. (1935). Berlin: Borntraeger.
KLEMM, W. & TILK, W. (1932). *Z. anorg. Chem.* **207**, 175.
PAULING, L. (1942). *The Nature of the Chemical Bond*, 2nd ed. Ithaca: Cornell University Press.
TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 842.
WELLS, A. F. (1938). *Z. Kristallogr.* **100**, 189.
WELLS, A. F. (1947). *Structural Inorganic Chemistry*, p. 508. Oxford: Clarendon Press.