The crystal and molecular structure of ammonium tetrachloroaurate(III) $\frac{2}{3}$ hydrate.

By M. BONAMICO and G. DESSY, *Laboratorio di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione del C.N.R., c/o Istituto Chimico, Università di Roma, Italy* and C. FURLANI and F. M. CAPECE, *Istituto Chimico, Università di Roma, Italy*

$NH_4AuCl_4.\frac{2}{3}H_2O$, grows as monoclinic prisms, space group $C2/c$, with $a = 14.054$ (10), $b = 11.519$ (5), $c = 14.496$ (10) Å, $\beta = 102.58$ (6)°; $Z = 12$ and $D_x = 3.2$ g cm^{-3}. Two crystallographically independent tetrachloroaurate ions are present in the unit cell; one lying on a twofold axis and the other on a general position. Coordination about the gold atoms is essentially square planar. The ammonium ions and water molecules form chains through the structure.

Introduction

Slow evaporation of an aqueous ethanol solution of NH_4AuCl_4 gave pale-yellow prisms of $NH_4AuCl_4.\frac{2}{3}H_2O$, which rapidly decompose in air under X-rays. Samples were therefore dipped in Nujol and sealed in Lindemann glass capillaries. The crystal size was approximately 0·10 mm across, μ(Cu $K\alpha$) = 489 cm^{-1}. Cell constants were determined by a modified version of Christ's method (Mazzone, Vaciago & Bonamico, 1963) from zero-layer Weissenberg films taken about the b and c axes (Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å). Space group $C2/c$ was determined from systematic absences and verified by the structure determination. Intensities of 1257 independent reflexions above film background (*ca.* 48% of those possible with Cu $K\alpha$ radiation) were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs. Corrections for Lorentz, polarization, spot extension, and cylindrical absorption effects were applied. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods with anisotropic thermal parameters to a final R value of 0·095. Final parameters are listed in Tables 1 and 2, and bond lengths and angles in Table 3.*

Table 3. *Bond distances and angles with their estimated standard deviations in parentheses*

Au(1)–Cl(1,1)	2·281 (7) Å
Au(1)–Cl(1,2)	2·254 (8)
Au(1)–Cl(1,3)	2·274 (9)
Au(1)–Cl(1,4)	2·283 (8)
Au(2)–Cl(2,1)	2·264 (8)
Au(2)–Cl(2,2)	2·253 (12)
O–N(1)	2·92 (3)
O–N(2)	2·90 (4)
Cl(1,1)–Au(1)–Cl(1,3)	91·2 (3)°
Cl(1,1)–Au(1)–Cl(1,4)	89·7 (3)
Cl(1,2)–Au(1)–Cl(1,3)	88·1 (3)
Cl(1,2)–Au(1)–Cl(1,4)	91·1 (3)
Cl(2,1)–Au(2)–Cl(2,2)	90·5 (5)

Results and discussion

Since $Z = 12$, there are two crystallographically independent molecules in the unit cell. The gold atom Au(1) is in

* The table of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30100. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final coordinates with standard deviations* ($\times 10^4$)

	x/a	y/b	z/c
Au(1)	596 (1)	694 (1)	8914 (1)
Au(2)	5000 (1)	823 (1)	7500 (1)
Cl(1,1)	2232 (6)	586 (7)	9528 (7)
Cl(1,2)	−1029 (6)	774 (7)	8347 (8)
Cl(1,3)	470 (7)	−1275 (8)	8887 (8)
Cl(1,4)	696 (6)	2672 (7)	8943 (8)
Cl(2,1)	3363 (6)	819 (7)	6955 (8)
Cl(2,2)	4806 (10)	839 (8)	9003 (8)
O	1708 (19)	3449 (24)	6547 (20)
N(1)	2500 (21)	2500 (27)	5000 (24)
N(2)	2948 (21)	3039 (27)	8390 (24)

Table 2. *Thermal parameters* (*with e.s.d.'s*)

b_{ij} is defined by: $T = \exp[-10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Au(1)	46 (1)	−13 (1)	16 (1)	77 (1)	−11 (2)	52 (1)
Au(2)	43 (1)	0	18 (2)	60 (1)	0	46 (1)
Cl(1,1)	51 (4)	−6 (8)	7 (8)	109 (7)	−6 (11)	73 (6)
Cl(1,2)	52 (4)	−12 (8)	34 (9)	95 (6)	−3 (11)	88 (7)
Cl(1,3)	75 (6)	−1 (9)	−16 (10)	92 (7)	26 (12)	86 (7)
Cl(1,4)	69 (5)	−18 (8)	34 (10)	86 (6)	−45 (12)	95 (8)
Cl(2,1)	54 (5)	−7 (8)	−1 (9)	97 (7)	12 (11)	86 (7)
Cl(2,2)	137 (9)	18 (13)	97 (13)	112 (8)	14 (13)	63 (6)

	$B(Å^2)$
O	6·60 (6)
N(1)	8·38 (10)
N(2)	5·60 (6)

SHORT COMMUNICATIONS

a general position and Au(2) lies on the twofold axis. Each gold atom is surrounded by four chlorine atoms in an approximately square planar arrangement. The maximum deviations from the least-squares planes are less than $0·02$ Å for both types of $[AuCl_4]^-$ ions. The planes of the two crystallographically independent ions are nearly orthogonal to one other. Table 2 shows that all the Au–Cl distances and the corresponding angles are equivalent within the standard deviations. The average Au–Cl bond length ($2·268$ Å) is in agreement with a dsp^2 covalent bond, as found in $AuCl_3$ (Clark, Templeton & MacGillavry, 1958). The Cl–Au–Cl angles are not significantly different from those expected ($90°$) for symmetrical square planar coordination of the trivalent gold atom. In the unit cell twenty possible sites were expected for the location of twelve NH_4^+ ions and eight H_2O molecules. Twenty regions with positive electron density were, in fact, found in a difference Fourier map, four on a centre of symmetry (with fourfold multeplicity), and the other sixteen in two general positions (with eightfold multiplicity). To determine which sites the ammonium ions occupied and which the water molecules, we examined the environment of these positions. In this way we have identified the ammonium ion in those positions surrounded by the maximum number of chlorine atoms. As may be seen in Fig. 1 the ammonium ions and the water molecules thus identified are alternate and connected by hydrogen bonds ($2·92$ Å) leading to the formation of five-membered chains. Four of the twelve ammonium ions located in this way were on a centre of symmetry. Since the ammonium ion is not centrosymmetric, the hydrogen atoms must be centre-disordered with 50% occupation, but the quality of the data does not permit the location of the hydrogen atoms. The non-centrosymmetric space group Cc does not require this concept of disorder for the NH_4^+ ions; however a refinement in this space group did not give any significant improvement in the R index (tested by use of Hamilton's (1965) R ratio).

The structure determination was undertaken in order to find a possible structural explanation for the 'spreading' of the experimental frequencies of the n.q.r. spectra of some tetrachloroaurate complexes. As pointed out by several workers (*e.g.* Scrocco, 1963) the halogen atoms occupying inequivalent positions in the elementary cell of the crystal give as many resonance frequencies as there are inequivalent positions. Alkali tetrachloroaurates have been widely investigated to this end (Caglioti, Furlani, Orestano & Capece, 1963; Fryer & Smith, 1970; Sasane, Matsuo, Nakamura & Kubo, 1971; Sartori, Capece & Furlani, 1967). NaAuCl$_4$.2H$_2$O known from previous structural investigation to have four inequivalent chlorine atoms (Bonamico, Dessy & Vaciago, 1965) does, in fact, exhibit four distinct n.q.r. lines between $25·4$ and $29·4$ MHz. After a preliminary report of only three frequencies (Caglioti, Furlani, Orestano & Capece, 1963), the fourth was discovered by more accurate measurements (Fryer & Smith, 1970; Sasane, Matsuo, Nakamura & Kubo, 1971), and identified by the anomalous temperature dependence of its frequency, as due to the hydrogen-bond perturbed Cl(1). All four lines of the Na compound appear throughout the range of temperature investigated by n.q.r. ($77-293°K$), and the frequency differences can be explained by the variation of the ionic character of the Au–Cl bond with distance, combined with the computed *efg* contributions from lattice neighbours (Sartori, Furlani & Capece, 1967).

NH$_4$AuCl$_4$.$\frac{2}{3}$H$_2$O is expected to give six n.q.r. ^{35}Cl lines,

all of which were observed (Sasane, Matsuo, Nakamura & Kubo, 1971) only in the intermediate temperature range $163-248°K$ (again in the frequency range $26-28$ MHz). Line intensities are strongly temperature dependent, and two of the six lines [presumably those due to the pairs of equivalent chlorines Cl(2,1)–Cl(2,1)^{IV} and Cl(2,2)–Cl(2,2)^{IV}] disappear above approximately $250°K$ [in fact, only four lines were reported at room temperature by Caglioti, Orestano, Furlani & Capece (1963)], and (all with one possible exception) disappear below $163°K$. Although an accurate one-to-one assignment is not possible, we conclude that the maximum number of observed n.q.r. frequencies again coincides with the number of crystallographically inequivalent resonant nuclei. There is, however, clear evidence that in some instances expected lines may not be found experimentally, probably owing to unfavourable lattice relaxation conditions, which may depend strongly on temperature and possibly on hydrogen-bonding effects. Caution has therefore to be used in deducing the number of inequivalent sites from experimental n.q.r. frequencies. A similar situation holds for KAuCl$_4$, where only four distinct frequencies were found between 27 and 28 MHz (Caglioti, Furlani, Orestano & Capece, 1963) and confirmed later (Sasane, Matsuo, Nakamura & Kubo, 1971), against eight inequivalent sites (Bonamico & Dessy, 1973). For this case, we assume that four of the eight expected frequencies are smeared out or reduced to nonobservable intensity. The alternative explanation of pair-wise coincidence of all eight frequencies appears improbable, unless an equalisation of the *efg*'s of pairs of *trans*-chlorines can be induced by appropriate molecular vibrations of the $[AuCl_4]$ chromophores.
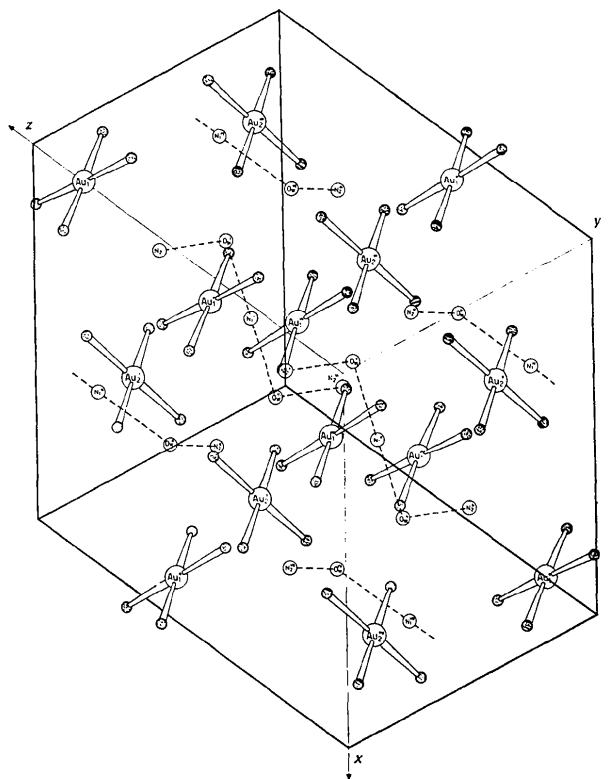

Fig. 1. Unit cell viewed along the [111] direction.

References

BONAMICO, M. & DESSY, C. (1973). *Acta Cryst.* B**29**, 1735–1736.

BONAMICO, M., DESSY, G. & VACIAGO, A. (1965). *Atti Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat.* **39**, 504–509.

CAGLIOTI, V., FURLANI, C., ORESTANO, F. & CAPECE, F. M. (1963). *Atti Accad. Nazl. Lincei Classe Sci. Fis. Mat. Natur. Rend.* **35**, 10–11.

CLARK, E. S., TEMPLETON, D. H. & MACGILLAVRY, C. H. (1958). *Acta Cryst.* **11**, 284–288.

FRYER, C. W. & SMITH, J. A. S. (1970). *J. Chem. Soc. (A),* pp. 1029–1035.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

MAZZONE, G., VACIAGO, A. & BONAMICO, M. (1963). *Ric. Sci.* **33**(IIA), 1113–1117.

SARTORI, G., CAPECE, F. M. & FURLANI, C. (1967). International Summer School on Theoretical Chemistry, n.q.r. Spectroscopy, Frascati (Rome).

SASANE, A., MATSUO, T., NAKAMURA, D. & KUBO, M. (1971). *J. Magn. Resonance,* **4**, 257–273.

SCROCCO, E. (1963). *Advanc. Chem. Phys.* **5**, 319–352.

A priori, for estriol, $\varphi_{200} = 0$ or π. By RICHARD D. GILARDI, *Laboratory for the Structure of Matter, Naval Research Laboratory, Washington D.C., U.S.A.*

The determination of $\varphi_{200} = 0$ for estriol is re-examined. It is easy to show, from a consideration of the structure-factor equations or by test calculation, that $\varphi_{200} = \pi$ is also consistent with the data. Therefore, the method of determination should not be considered definitive.

In a recent note by Hauptman (1972) entitled 'For estriol, $\varphi_{200} = 0$', a rationale was presented for the choice $\varphi_{200} = 0$ rather than $\varphi_{200} = \pi$ in the solution of the estriol structure (Hauptman, Fisher, Hancock & Norton, 1969). The argument was based upon the following: (*a*) the estriol molecules are approximately planar; (*b*) $|E_{200}| = 5{\cdot}40$, which is very large, but not near the theoretical maximum ($\sim 9{\cdot}2$); (*c*) $|E_{100}| = 0{\cdot}00$. If the two molecules of the asymmetric unit were lying near the $x = 0$ and $x = \frac{1}{2}$ planes, respectively, ensuring a large modulus and a zero phase for E_{200}, the atoms which were off the planes would make only small, second-order contributions to E_{100}, as expressed by Hauptman's equation (9):

$$E_{100} \simeq - \frac{1}{\sqrt{84}} \left\{ \sum_{1=\mu}^{21} \varepsilon_\mu^2 - \sum_{\mu=22}^{42'} \varepsilon_\mu^2 \right\}. \qquad (1)$$

Moreover, the above structure-factor equation expresses the difference between two summations of small positive quantities, and they could cancel one another.

Alternatively, if the molecules are almost coincident with the planes $x = \frac{1}{4}$ and $x = -\frac{1}{4}$ (which would give $\varphi_{200} = \pi$), the atoms would be lying near nodes of the trigonometric portion of the E_{100} structure-factor equation, and any deviations of atoms from the planes would contribute in a linear fashion to $|E_{100}|$. Hauptman's equation (10) expresses this hypothetical situation:

$$E_{100} \simeq \frac{2}{\sqrt{84}} \left\{ \sum_{\mu=1}^{21} \varepsilon_\mu - \sum_{\mu=22}^{42} \varepsilon_\mu \right\}. \qquad (2)$$

The individual contributors are first-order quantities, and are thus larger than the terms in the first equation. However, the ε_μ's are independent and have varying signs, in contrast to the ε_μ^2 in equation (1) which must all be positive; the ε_μ may cancel one another within the summations and this can overrule the argument that the ε_μ are larger quantities. Thus, it is not 'clear' (as Hauptman states) that the right-hand side of equation (1) is more consistent with a value of zero than that of equation (2). One could not have said, given this situation, that φ_{200} was definitely zero.

To check this analysis of the problem, a test calculation was performed on estriol. Using the published coordinates for the non-hydrogen atoms from Table 2*a* of Cooper, Norton & Hauptman (1969) and the point-atom structure formulae for E_{200} and E_{100} given by Hauptman (1972), structure factors were calculated with the estriol molecules at varying positions in the unit cell. With no shift, $E_{200} = +6{\cdot}46$ and $E_{100} = +0{\cdot}05$; these values agree well with the experimentally derived moduli. If molecule I is shifted by $r = -0{\cdot}24a$, and molecule II is shifted by $r = -0{\cdot}265a$, the resultant values are $E_{200} = -6{\cdot}51$ and $E_{100} = +0{\cdot}00$. No *a priori* packing arguments could rule out this possible trial structure; it is possible that other available structure-factor information might do so. There are many other possible combinations of shifts which yield a similar result, namely, $\varphi_{200} = \pi$.

Note added in proof: The intent of this note is to demonstrate that Hauptman's (1972) analysis was not definitive and to imply that the probability of the alternative conclusion ($\varphi_{200} = \pi$) may be significant. Hauptman has since provided me with an *a posteriori* calculation on estriol which, although quite approximate, estimates this probability to be in the 10 to 20% range. This estimate is not directly related to the point in question, namely, the *a priori* probability, since it is based on known structural parameters. Moreover, because the calculation explores only a limited number of packing arrangements, its applicability to the estriol case is difficult to assess. However, even accepting these estimates as correct, they support the conten-