

The Di-Aquo Proton in Hydrogen Tetracyanoaurate(III) Dihydrate*

BY R. A. PENNEMAN AND R. R. RYAN

University of California, Los Alamos Scientific Laboratory, Los Alamos, NM 87544, U.S.A.

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The crystal structure of $\text{HAu}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ has been determined by a three-dimensional X-ray study. The crystals are monoclinic, space group $P2_1/c$ with $a=7.881(5)$, $b=10.129(4)$, $c=6.798(3)$ Å, $\beta=123^\circ 19(2)'$, for $z=2$, $d_x=2.48$, d_m (flotation) $=2.45(2)$ g.cm⁻³. The structure was refined by full-matrix least-squares methods, using 646 observed reflections, to an unweighted R value of 0.043. The structure consists of square-planar gold tetracyanide ions linked by H_5O_2^+ ions. In this latter unit, the O—O distance is quite short, 2.47Å , as is characteristic of the di-aquo proton. The two oxygen atoms in the H_5O_2^+ unit are centered across a crystallographically imposed $\bar{1}$ site; the H_5O_2^+ ion is inferred to be in the *trans* conformation from the positions of the nitrogen atoms which are hydrogen-bonded at distances of 2.71 and 2.75 Å.

Introduction

Some years ago, Jones & Penneman (1954) studied the cyano complexes of monovalent Ag and Au by means of infrared spectroscopy and later extended the study to include those of Au(III). During the course of the later study, the strong acid $\text{HAu}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ was prepared (Smith, Jones, Kressin & Penneman, 1965).

Monohydrates of strong acids in which the hydronium ion (or singly hydrated proton, H_3O^+) occurs are well known, and in recent years several structures containing the well-defined di-aquated proton, H_5O_2^+ , have been found. This ion was apparently first suggested in a paper by Huggins (1963). For a recent review, see Williams (1969) and papers by Olovsson (1968) and by Lundgren & Olovsson (1967). It was thus of interest to determine the disposition of the two water atoms per proton in $\text{HAu}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$. The compound is interesting in itself, being a stable, strong acid in contrast to $\text{HAu}(\text{CN})_2$, which is markedly unstable and loses HCN readily.

Experimental

The free acid $\text{HAu}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ was prepared as a colorless microcrystalline powder by evaporating to dryness the effluent obtained after passing aqueous $\text{KAu}(\text{CN})_4$ through H^+ -form Dowex-50 resin (Smith *et al.*, 1965). After air drying, analysis for H, Au, C, and N established the formula as $\text{HAu}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$. Attempts to produce single crystals of $\text{HAu}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ by recrystallizing this finely divided material from water led to the following difficulty: clear crystals were retained only while in contact with the mother liquor;

they rapidly turned cloudy when exposed to air. An unstable higher hydrate is probably responsible. However, $\text{HAu}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ is very soluble in amyl acetate, and recrystallization yields clear, stable crystals that give the correct analysis for $\text{HAu}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ and are suitable for a single-crystal X-ray study.

Optical examination showed that the crystals were biaxial with large $2V(-)$ and thus were of orthorhombic or lower symmetry. Precession photographs of several crystals established monoclinic symmetry, space group $P2_1/c$, with extinctions: $h0l$, $l=2n+1$; $0k0$, $k=2n+1$; and hkl no restrictions, but reflections of the type $k+l=2n$ were very strong compared to those of $k+l=2n+1$. This implies that the heavy atom is A -centered, which is consistent with space group considerations (for $z=2$).

A single crystal of approximate dimensions $0.07 \times 0.14 \times 0.15$ mm was used for data collection. The cell constants were determined by least-squares refinement, using as observations the setting angles of 12 high-order reflections that had been centered on an automated four-circle Picker X-ray diffractometer using $\text{Mo } K\alpha_1$ radiation ($\lambda=0.70930$ Å). The values thus determined are: $a=7.881(5)$, $b=10.129(4)$, $c=6.798(3)$ Å and $\beta=123^\circ 19(2)'$. The calculated density for $Z=2$ is 2.48 g.cm⁻³; the density measured by flotation is 2.45 ± 0.02 g.cm⁻³.

Intensity data were collected on a Picker diffractometer, using $\text{Mo } K\alpha$ radiation, a single-crystal graphite monochromator (using the 002 reflection), and a take off angle of 5° . The count was taken using a θ - 2θ scan over a 2θ range of 2° (plus the α_1 - α_2 dispersion) with 0.05° steps for 2 sec at each step; stationary-counter stationary-crystal background counts of 20 sec were taken at each end of the scan. Intensities were collected for hkl , $\bar{h}kl$, and some $\bar{h}k\bar{l}$ planes up to values of $2\theta \leq 55^\circ$. Of the 1283 reflections measured, 1037 remained after

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averaging equivalent reflections and 646 were judged to be observed according to the criterion $I \geq 3\sigma(I)$, where $\sigma^2(I) = f^2(t)(T+B) + \sigma_s^2(T-B)^2$, T being the total count, B the estimated background, and $f(t)$ the time-dependent correction factor discussed below. The quantity σ_s^2 was taken to be 2.5×10^{-4} , a number which we feel to be a reasonable estimate of the normalized variance of a reflection due to random variations other than counting statistics.

The intensity of a standard reflection was measured after every 20 reflections. The final intensity of the standard reflection was 60% of its starting value. The alignment of the crystal was examined periodically. Multiplicative correction factors $[f(t)]$ for the data were determined by least-squares methods, fitting a fifth-order polynomial to the intensity measurements of the standard reflection. The order of the polynomial was determined from significance tests based on the sum-of-the-squares of the residuals (Hamilton, 1965). Corrections were made for the Lorentz and polarization factors. The graphite crystal in the monochromator was assumed to be of perfect mosaicity, giving the following form for the polarization factor: $(\cos^2 2\alpha + \cos^2 2\theta)/(1 + \cos^2 2\alpha)$, where α is the angle the beam makes with the monochromator. The absorption corrections were made by the Busing & Levy (1957) method, using Burnham's (1962) program as modified by Larson, Cromer & Roof (1964). The linear absorp-

tion coefficient for Mo $K\alpha$ radiation is 167 cm^{-1} , and the calculated transmission varied from 0.10 to 0.3.

The Patterson function showed all the heavy-atom-light-atom vectors to be resolved, and a chemically reasonable structure could be deduced directly from it. The Patterson function is, however, a superposition of the structure as seen from the 0, 0, 0 and the 0, $\frac{1}{2}$, $\frac{1}{2}$

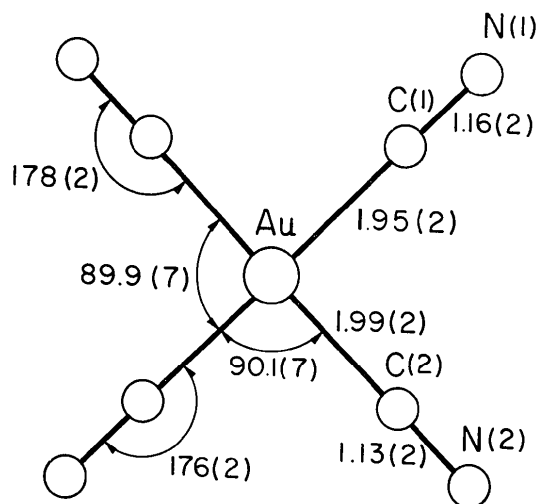


Fig. 2. Distances and angles in $\text{Au}(\text{CN})_4^-$.

Table 1. Fractional coordinates and thermal parameters (all $\times 10^4$)

Thermal parameters are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	6069 (16)	4029 (12)	5304 (20)	247 (27)	70 (13)	329 (44)	-39 (32)	293 (60)	-11 (40)
Au	0	5000	5000	126 (2)	93 (1)	207 (3)	3 (6)	120 (3)	54 (8)
C(1)	982 (22)	-848 (19)	3017 (29)	157 (34)	112 (21)	214 (56)	-31 (47)	122 (72)	-93 (61)
C(2)	2156 (23)	1362 (18)	1618 (26)	202 (37)	121 (23)	187 (50)	-1 (50)	211 (75)	-124 (58)
N(1)	1623 (21)	-1279 (18)	4880 (29)	259 (39)	144 (24)	303 (60)	-14 (49)	227 (82)	-1 (63)
N(2)	3408 (19)	2110 (17)	2592 (28)	201 (33)	136 (23)	366 (59)	-42 (46)	198 (76)	-177 (64)

Extinction factor, $g = (4 \pm 1) \times 10^{-6}$.

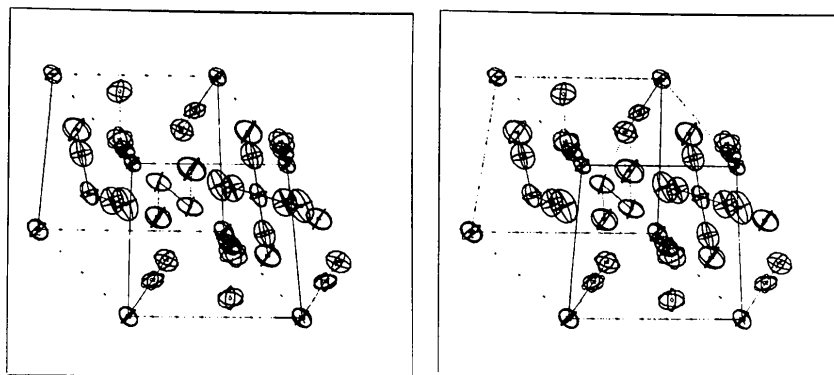


Fig. 1. Stereo view showing the oxygen atoms of the H_5O_2^+ unit linked to the nearest cyanide nitrogen atoms by dotted lines. Only one complete $\text{Au}(\text{CN})_4^-$ ion is shown.

Au positions. In order to prejudice the results as little as possible we calculated a difference map phased on the gold and one cyanide, which enhanced the image of one structure relative to the other. The structure thus determined was refined using Larson's (1970) full-matrix least-squares program. The function minimized was $\sum w_i(|F_o| - |F_c^*|)^2$, where w_i is the weight defined as

$$1/\sigma^2(F_o) \text{ and } F_c^* = kF_c / \left\{ 1 + g \text{Lp} \left[\frac{2(1 + \cos^4 2\theta)}{(1 + \cos^2 2\theta)^2} \right] F_c^* \right\}^{1/2}$$

in which k is a scale constant, Lp is the Lorentz-polarization factor, g is the extinction coefficient (Zachariasen, 1963; Larson, 1967), and F_c is the structure factor calculated in the usual way. Structure factors were calculated using the neutral atom scattering factors of Doyle & Turner (1968) with appropriate dispersion corrections for gold (Cromer & Liberman, 1970). The final R value ($R = \sum(|F_o| - |F_c^*|) / \sum|F_o|$) was 0.043 when anisotropic temperature factors and an extinction correction were included. A final difference Fourier map failed to show meaningful positions for the hydrogen atoms.

Table 2. *Interatomic distances and angles*

O—O	2.47 (2) Å	O—O—Au	108.9 (6)°
O—Au	3.36 (1)	O—O—N(1)	103.5 (7)
O—N(1)	2.75 (2)	O—O—N(2)	104.8 (7)
O—N(2)	2.72 (2)	N(1)—O—N(2)	119.2 (7)
Au—C(1)	1.95 (2)	C(1)—Au—C(2)	89.9 (7)
Au—C(2)	1.99 (2)	C(2)—Au—C(1)	90.1 (7)
C(1)—N(1)	1.16 (2)	N(1)—C(1)—Au	176 (2)
C(2)—N(2)	1.13 (2)	N(2)—C(2)—Au	178 (2)

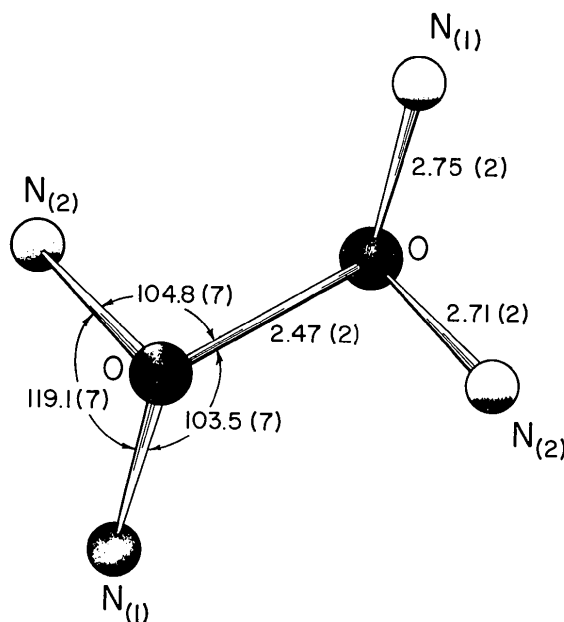


Fig. 3. Distances and angles involving the H_5O_2^+ ion and the nearest nitrogen atoms.

The atomic parameters for $\text{H}_5\text{O}_2 \text{Au}(\text{CN})_4$ are listed in Table 1 and the interatomic distances and angles in Table 2. Table 3 lists the observed and calculated structure factors. A stereo view of the structure is shown in Fig. 1, where dotted lines indicate hydrogen bonding. Fig. 2 displays the distances and angles in the planar $\text{Au}(\text{CN})_4^-$ ion, and the inferred geometry of the H_5O_2^+ ion is presented in Fig. 3.

Discussion

The $\text{Au}(\text{CN})_4^-$ ion has, within the limits of error of the experiment, idealized symmetry D_{4h} . That is to say, the C—Au—C angles are 90° , the Au—C—N groups are linear, and the relevant distances are equivalent.

The Au—C bond length in $\text{Au}(\text{CN})_4^-$ is somewhat shorter than observed in the gold(III)—C(alkyls) and in $\text{Au}(\text{CN})_2^-$ (2.1 Å) (Rosenzweig & Cromer, 1959). Jones and Smith (1964) found that the Au—C force constant is greater for $\text{Au}(\text{CN})_4^-$ than for $\text{Au}(\text{CN})_2^-$. Their vibrational analysis of $\text{Au}(\text{CN})_4^-$ indicated little metal ligand π -bonding but a very strong Au—C σ -bond.

In the structure of $\text{H}_5\text{O}_2 \text{Au}(\text{CN})_4$, the square-planar $\text{Au}(\text{CN})_4^-$ ions are linked through the nitrogen atoms by hydrogen bonds from an isolated H_5O_2^+ ion, which is centered in the cell across the $\bar{1}$ site at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (see Fig. 1). The arrangement of atoms around each of the oxygen atoms in H_5O_2^+ is very nearly tetrahedral. The O—O—N(1) and O—O—N(2) angles are $103.5 (7)$ and $104.8 (7)^\circ$ respectively, and the O—O—Au angle is $108.9 (6)^\circ$. This suggests strongly that the lone pair on the oxygen atom is oriented toward the gold. The O—O unit is sandwiched between two planar $\text{Au}(\text{CN})_4^-$ ions. This H_5O_2^+ ion has the typically short O—O distance of 2.47 Å, as has been established in several compounds which contain it (Williams & Peterson, 1969; Williams, 1969; Lundgren & Olovsson, 1967). *Ab initio* M. O. calculations by Kollman & Allen (1970) indicate that substantial energy is involved in the hydration of the hydronium ion, e.g., $\text{H}_3\text{O}^+ + \text{H}_2\text{O} = \text{H}_5\text{O}_2^+$, 37 kcal.mole $^{-1}$. Of three different geometrical arrangements, Kollman & Allen calculated that the least stable configuration around the H_5O_2^+ ion was tetrahedral. However, in $\text{H}_5\text{O}_2 \text{Au}(\text{CN})_4$ it is clearly the tetrahedral configuration which is present. The H_5O_2^+ ion has been found to be tetrahedral (sp^3) in some structures (Olovsson 1968; Williams & Peterson, 1969) but staggered (sp^2) in others (Lundgren & Olovsson, 1967). An important stabilizing force in our structure may well be the orientation of the lone pair on the oxygen atom toward the gold at just the tetrahedral angle.

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References

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