

(*tert*-Butyl isocyanide)chlorogold(I)

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Abstract. AuCl(C₃H₇N), $M_r = 315.55$, orthorhombic, *Pnma*, $a = 12.966(2)$, $b = 6.615(1)$, $c = 9.730(2)$ Å, $V = 834.6$ Å³, $Z = 4$, $D_x = 2.511$ g cm⁻³, Mo $K\alpha$, $\lambda(K\alpha_1) = 0.70926$, $\lambda(K\alpha_2) = 0.71354$ Å, $\mu = 178.36$ cm⁻¹, $F(000) = 568$, $T = 293$ K, $R = 0.036$, $wR = 0.045$ for 678 observations. An improved synthesis of this complex is reported. The molecule lies on a crystallographic mirror plane and the coordination environment of gold(I) is linear, two coordinate. The relatively short gold–carbon(isocyanide) bond of 1.92(1) Å may indicate significant gold–ligand back-bonding. There are no unusually short intermolecular contacts indicative of gold–gold bonding.

Introduction. The utility of gold compounds for the treatment of rheumatoid arthritis has been known for some time (Forestier, 1929). More recently, the (triethylphosphine)gold(I) tetraacetylthioglucose complex auranofin has been found to exhibit oral activity and, as with other gold drugs, inhibits the progressive advance of this degenerative disease (Sutton, McGusty, Walz & DiMartino, 1972; Sutton, 1983; Blodgett, Heuer & Pietrusko, 1984). During our studies on the mechanism of action of this class of gold(I) complexes we were intrigued by complexes containing other strongly bound ligands especially those ligands capable of backbonding interactions with the metal center. Alkyl isocyanides have binding constants comparable to those of alkylphosphines (Roulet & Favez, 1975) and may be less readily metabolized (alkylphosphines are readily oxidized to the relatively weakly coordinating corresponding phosphine oxide). To this end a series of isocyanide gold complexes were synthesized. We report here an improved synthesis for and the crystal and molecular structure of (*tert*-butyl isocyanide)-chlorogold(I).

Experimental. Synthesis of the title compound was first reported by McCleverty & DeMota (1973) in 29% yield. We have obtained the complex in 49% yield by the following modified procedure:

A solution of *tert*-butyl isocyanide (4.0 ml, 0.035 mol) in absolute ethanol (30 ml) was added

slowly at room temperature to a stirring solution of chloroauric acid monohydrate (10.0 g, 0.028 mol) in absolute ethanol (140 ml) under nitrogen. Some solid formed during the addition and the resulting yellow mixture was stirred for 1 h at room temperature. Another portion of *tert*-butyl isocyanide (4.0 ml, 0.035 mol) in absolute ethanol (30 ml) was added over a 10 min period and then stirred for an additional 20 min. The off-white solid product was collected by suction filtration, washed with cold absolute ethanol (10 ml) and dried *in vacuo* at room temperature to give the crude product (5.53 g). A second crop was obtained from the mother liquor (0.77 g). Both crops were combined and recrystallized from absolute ethanol (160 ml) to give white needles (4.3 g, 48.8% yield, m.p. 439–441 K). The recrystallized product was characterized satisfactorily by ¹H NMR, TLC, IR, UV and elemental analysis.

Approximate crystal dimensions 0.30 × 0.50 × 0.30 mm mounted in quartz capillary with longest dimension parallel to ϕ . Enraf–Nonius CAD-4 diffractometer, graphite monochromator; systematic absences $0kl$ for $k + l$ odd, $hk0$ for h odd; cell constants from least-squares analysis of setting angles for 25 reflections with $30 \leq 2\theta(\text{Mo}) \leq 35^\circ$ measured on diffractometer. Intensity data collected in 2θ scan mode, as suggested by peak-shape analysis; 1150 measured intensities, $2\theta \leq 55^\circ$, $0 \leq h \leq 12$, $0 \leq k \leq 8$, $0 \leq l \leq 16$; Lorentz–polarization correction, absorption correction based on ψ scans of nine reflections with $80 \leq \chi \leq 90^\circ$, correction factor: min. = 0.6468, max. = 0.9986; no systematic fluctuations in reflections $\bar{2}, 1, 10, 245, 328$ monitored at beginning, end and each 3 h during data collection (5 times); max. deviations in F 0.83, 1.28 and 0.48%, respectively; mean values of F 181.9 (9), 157.0 (8) and 253.70 (8), respectively. Programs in CAD-4 *SDP* with local modifications. Position of gold atom located from Patterson map; found, as expected, to lie on crystallographic mirror plane; y coordinate of gold atom fixed at $\frac{1}{4}$; remaining non-hydrogen atoms located from difference Fourier synthesis; anisotropic least-squares refinement (on F) of positions led to $wR = 0.058$; $w = 4F_o^2/\sigma^2(I)$; subsequent difference Fourier synthesis revealed positions for all hydrogens; however, hydrogens held at fixed positions assuming

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C—H bond length of 1.0 Å and assigned fixed isotropic temperature factors of 7.0 Å² in final refinement cycles. Four final cycles, weighting scheme above with $\sigma(I)$ as defined by Corfield, Doedens & Ibers (1967) with $p = 0.04$, $wR = 0.045$, $S = 1.37$, 678 observations with $I \geq 4.0\sigma(I)$, 47 variables; extinction parameter included in later stages refined to $5.3(1) \times 10^{-7}$. In final least-squares cycle max. $\Delta/\sigma = 0.02$; final difference Fourier map contained four regions of positive density (max. heights 1.42 to 1.18 e Å⁻³) nearly equidistant from and in a square-planar arrangement about the Au atom; max. negative densities of heights -0.13 to -0.09 e Å⁻³. Refinement using 911 observations with $I \geq 0.01\sigma(I)$ gave $R = 0.050$. Refinement in non-centrosymmetric space group $Pn2_1a$ failed to improve structural model as judged by residual values and improbable carbon-carbon bond lengths. This later refinement also failed to converge. Neutral-atom scattering factors and effects of anomalous dispersion for nonhydrogen atoms from *International Tables for X-ray Crystallography* (1974), for H atoms from Stewart, Davidson & Simpson (1965).

Discussion. The positional parameters along with their standard deviations as estimated from the inverse matrix are listed in Table 1.* The structure of a single molecule is displayed in Fig. 1. Atoms Au, Cl, C(1), N(1), C(2) and C(3) all lie on a crystallographic mirror plane. Principal bond lengths and angles are given in Table 2. The coordination environment of gold is linear and the Au—Cl bond distance of 2.249 (3) Å is typical of Au^I-chloride bonds (Jones, 1981). The Au—C(1) distance of 1.92 (1) Å is substantially shorter than distances observed in the methyl isocyanide complex (NC)—Au—CNCH₃, in which the Au—C(cyanide) distance is 2.01 (5) Å and the Au—C(isocyanide) distance is 1.98 (5) Å (Esperas, 1976) and also contrasts with the Au—C distance of 2.12 (3) Å reported for the structure of (Ph)₃P—Au—CH₃. The shorter Au—C bond observed for the *tert*-butyl isocyanide structure may reflect more effective Au—isocyanide backbonding for this ligand, which is *trans* to a σ -only donor chloride. Similarly, the Au—C distance of 1.94 (2) Å reported for the structure of (isopropylamine)(phenylethynyl)Au^I (Corfield & Shearer, 1967) is consistent with this explanation.

The C(1)—N(1) triple-bond distance of 1.13 (2) Å is consistent with values reported in related cyano and isocyanide complexes. The isocyanide ligand is linear with both Au—C(1)—N(1) and C(1)—N(1)—C(2) bond angles of 179 (1)°.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42483 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and thermal parameters*

| | x | y | z | $B_{eq}(\text{Å}^2)^\dagger$ |
|--------|--------------|-----------|--------------|------------------------------|
| Au | -0.01804 (4) | 0.250* | -0.08115 (6) | 4.51 (1) |
| Cl | 0.1268 (3) | 0.250* | -0.2083 (5) | 6.7 (1) |
| N(1) | -0.2218 (9) | 0.250* | 0.075 (1) | 4.8 (3) |
| C(1) | -0.146 (1) | 0.250* | 0.018 (2) | 5.0 (3) |
| C(2) | -0.319 (1) | 0.250* | 0.151 (2) | 5.4 (3) |
| C(3) | -0.293 (1) | 0.250* | 0.300 (2) | 8.3 (6) |
| C(4) | -0.3784 (9) | 0.061 (2) | 0.108 (1) | 7.1 (3) |
| H1C(3) | -0.364* | 0.250* | 0.355* | 7.0* |
| H1C(4) | -0.359* | 0.060* | 0.011* | 7.0* |
| H2C(3) | -0.258* | 0.373* | 0.325* | 7.0* |
| H2C(4) | -0.335* | -0.061* | 0.134* | 7.0* |
| H3C(4) | -0.445* | 0.050* | 0.165* | 7.0* |

* Held fixed in the refinement.

† $B_{eq} = \sum_i \sum_j a_i a_j \beta_{ij}$.

Table 2. *Principal bond lengths (Å) and angles (°)*

| | | | |
|----------------|-----------|----------------|-----------|
| Au—Cl | 2.249 (3) | Au—C(1) | 1.92 (1) |
| N(1)—C(1) | 1.13 (2) | N(1)—C(2) | 1.47 (2) |
| C(2)—C(3) | 1.49 (2) | C(2)—C(4) | 1.52 (1) |
| Cl—Au—C(1) | 176.7 (5) | C(1)—N(1)—C(2) | 179 (1) |
| Au—C(1)—N(1) | 179 (1) | N(1)—C(2)—C(3) | 107 (1) |
| N(1)—C(2)—C(4) | 107.2 (7) | C(3)—C(2)—C(4) | 112.3 (8) |

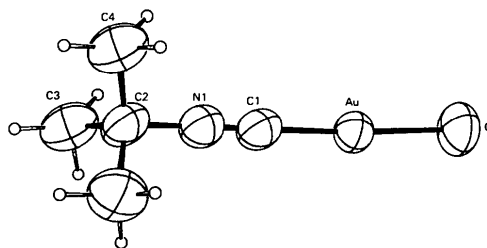


Fig. 1. View of a single molecule of (*tert*-butyl isocyanide)-chlorogold(I) showing the labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. H atoms shown as small spheres of arbitrary size.

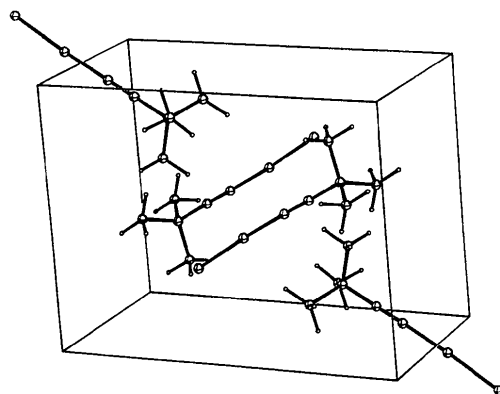


Fig. 2. Unit-cell packing diagram for (*tert*-butyl isocyanide)-chlorogold(I); c axis is vertical, a axis is horizontal.

A diagram of the unit-cell packing is presented as Fig. 2. The molecules stack pairwise such that Au of one molecule sits approximately above (or below) the C(1)–N(1) triple bond. The closest approach of Au atoms is 3.695 (1) Å indicating no Au–Au bonding within this structure.

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Potassium Salt of 1,4-Dihydro-4,4-dimethoxy-5,7-dinitrobenzofurazan-3-oxide with Methanol:* a Meisenheimer Complex of 4,6-Dinitrobenzofuroxan

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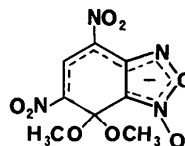
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Abstract. $C_8H_7N_4O_8 \cdot K^+ \cdot CH_3OH$, $M_r = 358.29$, triclinic, $P\bar{1}$, $a = 7.463$ (1), $b = 9.723$ (2), $c = 10.378$ (2) Å, $\alpha = 79.41$ (2), $\beta = 87.08$ (2), $\gamma = 72.21$ (2)°, $V = 704.8$ (2) Å³, $Z = 2$, $D_x = 1.69$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 4.87$ cm⁻¹, $F(000) = 368$, room temperature, $R = 0.069$ for 1325 reflections with $F_o^2 > 3\sigma(F_o^2)$. The geometry of the furoxan ring of the title compound is the same as previously observed in benzofuroxan and 4,6-dinitrobenzofuroxan. The distortion from planarity and the sequence of long and short bonds in the ring of the title compound, caused by the presence of the alkoxy groups, follow the same pattern observed in a related Meisenheimer complex of dinitrobenzofurazan.

Introduction. During previous studies of σ complexes of benzofuroxan, compound (I) was characterized in solution by NMR (Buncel, Chuaqui-Offermanns, Moir & Norris, 1979). However, the NMR assignment of the structure is equivocal as the molecule can rearrange, changing the position of the furoxan O atom. W. P. Norris isolated the Meisenheimer complex (I) as its K salt (Norris, Chafin, Spear & Read, 1984). To determine the position of the O in the solid state and to understand better the chemical reactivity of this molecule, we now report the crystal structure of the K

salt. (I) is compared with other benzofuroxans and benzofurazans.



(I)

Experimental. Suitable orange, euhedral crystals were obtained from methanol. Crystal for data collection approximately 0.10 × 0.20 × 0.32 mm. Prior to initiating the structure determination, it was determined that these crystals evolved at 377 K one molecule of CH₃OH per molecule of the Meisenheimer complex. Unit-cell parameters determined by a least-squares fit of 24 computer-centered reflections with 2θ values ranging from 6 to 24° (Mo $K\alpha$). 2103 intensity data for the octants $\bar{h}\bar{k}l$, $\bar{h}kl$, $h\bar{k}l$, hkl to 45° (2θ) (with values of $h = -9$ to $+9$, $k = -11$ to $+11$, and l 0 to $+12$) were collected on a Nicolet R3 diffractometer with monochromatized Mo $K\alpha$ radiation using $2\theta/\theta$ scans and variable scan speeds from 2 to 10° (2θ) min⁻¹. Total time spent collecting backgrounds at each end of a scan was 50% of the scan time. Scan range from 1° < $K\alpha_1$ (2θ) to 1° > $K\alpha_2$ (2θ). Intensity data for three check reflections

* Current *Chemical Abstracts* name.