Synthesis, Characterization and Structure of Tribromo(2-phenyl-1,8-naphthyridine)gold(III)

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Neutral tribromo(2-phenyl-1,8-naphthyridine)gold(III), $AuBr_3$(N-N), has been prepared by reaction of $KAuBr_4$ with the ligand in $CHCl_3/C_2H_5OH$ and was characterized by ^{1}H NMR spectroscopy and X-ray diffraction. The molecular and crystal structure of $AuBr_3$(N-N) · 0.5 THF (triclinic, $P\bar{1}$, a = 11.314(2), b = 12.350(3), c = 14.628(3) Å, α = 107.96(3), β = 98.86(3), γ = 107.29(3)°, Z = 4, 173 K) shows coordination of the N^8 nitrogen atom situated in the unsubstituted pyridine ring to the planar four-coordinate Au^{III} center. Whereas the $AuBr_3N$ best planes and the coordinated naphthyridine rings are not far from orthogonal ($\omega \sim 105°$), the phenyl substituents were found in the crystal with a *ca.* 22° dihedral angle relative to the naphthyridine plane. Intermolecular Au···Br distances close to the sum of the van der Waals radii indicate very weak interactions to form a quasi-dimeric arrangement in the crystal.

Key words: Crystal Structure, Gold Complexes, Naphthyridine Ligands, Intermolecular Interactions

Introduction

Gold-containing catalysts have been successfully used in organic synthesis [1 – 4]. In these applications, complexes with gold in the oxidation states I or III and with different ligands have been introduced as precatalysts. Gold(III) compounds containing nitrogen donor ligands have shown good results regarding the activity and/or selectivity to produce organic products of interest.

Neutral gold(III)/nitrogen donor complexes have been studied with regard to the roles of ligand proton affinity and π-bonding in the gold-nitrogen interaction for a variety of heterocyclic nitrogen donor ligands [5]. Recent research has also shown that gold(III) compounds featuring approximately planar geometries (as found in cisplatin) may target DNA and act as new anti-tumor agents [6]. In addition, coordination compounds of noble metals with d^6 or d^8 electronic configuration have electronically excited states with long-lived luminescence [7, 8] which is also a characteristic of many gold complexes. Finally, suitable precursor complexes for gold nanoparticles have been sought recently [9].

Having in mind all these antecedents, we set out to synthesize gold(III) complexes which contain bidentate nitrogen donor ligands derived from 1,8-naphthyridine, specifically from 2-phenyl-1,8-naphthyridine (N-N), **1**. 2,7-Dimethyl-1,8-naphthyridine complexes of dimethylgold halides and pseudohalides have been reported and studied with respect to their fluxional behavior by Schmidbaur and Dash [10].

The reaction of potassium tetrabromoaurate(III) and 2-phenyl-1,8-naphthyridine produces a neutral gold(III) complex, $AuBr_3$(N-N) **2**, the characterization of which is described here.

Experimental Section

Instrumentation

^{1}H NMR spectra for the complex were run on a Bruker FT-NMR 400 MHz spectrometer. ^{1}H and ^{13}C NMR spectra of the 2-phenyl-1,8-naphthyridine ligand in both mono- and two-dimensional modes were registered with a Bruker Avance DRX 300 MHz spectrometer. Samples were studied

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in deuterated chloroform at r. t. Elemental analyses were carried out using a CE Instruments model EA 1108 elemental analyzer.

Syntheses

*2-Phenyl-1,8-naphthyridine, (N-N), (**1**)*

The compound was prepared from the reaction of 2-aminonicotinaldehyde [11] with acetophenone, an enolizable ketone, through a Friedländer condensation in alkaline ethanol. The ligand was characterized by ^{1}H NMR spectroscopy [12], showing the typical chemical shifts of a substituted 1,8-naphthyridine. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.10 (dd, 1H, H_7), 8.29 (m, 2H, H_{10} and H_{14}), 8.28 (d, 1H, H_3), 8.22 (dd, 1H, H_5), 8.02 (d, 1H, H_4), 7.55 (m, 3H, H_{11}, H_{12} and H_{13}), 7.47 (dd, 1H, H_6).

*$AuBr_3$(N-N) (**2**)*

To a solution of 2-phenyl-1,8-naphthyridine (38 mg, 0.18 mmol), dissolved in chloroform (5 mL), a solution of potassium tetrabromoaurate (100 mg, 0.18 mmol) in ethanol (15 mL) was added dropwise. The orange suspension obtained was heated for 3 h at 50 °C. The solution was filtered and the solid washed with ethanol. THF (30 mL) was then added to the solid, and the remaining insoluble material (KBr) was separated by filtration. Finally the volume of the solution was reduced and cooled to −30 °C which led to the crystallization of a red solid (yield 85 mg, 71 %) with some THF incorporated in the crystals. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.53 (dd, 1H, H_7, J = 5.3; 1.5 Hz), 8.85 (dd, 1H, H_5, J = 8.0; 1.5 Hz), 8.68 (d, 1H, H_3, J = 8.6 Hz), 8.56 (m, 2H, H_{10} and H_{14}), 8.48 (d, 1H, H_4, J = 8.6 Hz), 7.97 (dd, 1H, H_6, J = 8.0; 5.3 Hz), 7.64 (m, 3H, H_{11}, H_{13} and H_{12}). – Analysis for $C_{14}H_{10}AuBr_3N_2 \cdot 0.5$ THF (678.99): calcd. C 28.30, N 4.13, H 2.08; found C 27.50, N 4.10, H 1.95.

Crystal structure analysis

Single crystals were grown by cooling a hot THF solution of $AuBr_3$(N-N), **2**. When the solution reached r. t., the crystals were formed. The crystals were separated from the liquid phase by filtration and were dried under vacuum.

A suitable crystal was selected, attached to a glass fiber and instantly placed in a low-temperature N_2 stream and measured using MoK_α radiation (0.71073 Å). All data were collected at 173 K using a Siemens P4 diffractometer. Absorption effects were corrected empirically with the routine DELABS in PLATON [13]. The ADDSYM routine in PLATON as well as routines in OLEX2 [15] were used for intensive checks of additional symmetry elements, but no higher-symmetry space group was found. The structure was solved by Direct Methods using SHELXS in SHELXTL-PC [14] and completed (non-H atoms) by difference Fourier techniques. Refinement until convergence was obtained by full-matrix least-squares on F^2 using SHELXL-97 [14]. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The molecular graphics and the material for publication was generated using OLEX2 [15].

Table 1. Crystal data and structure refinement for $AuBr_3$(N-N) · 0.5 THF (**2**).

Formula	$C_{16}H_{14}AuBr_3N_2O_{0.5}$
M_r	678.99
Temperature, K	173(2)
Crystal size, mm^3	$0.43 \times 0.22 \times 0.18$
Crystal system	triclinic
Space group	$P\bar{1}$
a, b, c, Å	11.314(2), 12.350(3), 14.628(3)
α, β, γ, deg	107.96(3), 98.86(3), 107.29(3)
Volume, Å^3	1787.3(9)
Z	4
ρ_{calc}, g cm^{-3}	2.52
μ(MoK_α), mm^{-1}	14.9
F(000), e	1248
ϑ range for data collection, deg	1.52 – 55
Index ranges	$-6 \le h \le 14$, $-16 \le k \le 15$, $-19 \le l \le 18$
Refl. collected / indep. / R_{int}	8625 / 8205 / 0.1059
Data / restraints / parameters	8205 / 270 / 406
Final indices $R1/wR2$ [$I \ge 2\sigma(I)$]	0.0669 / 0.1539
Final indices $R1/wR2$ (all data)	0.1169 / 0.1806
Goodness-of-fit on F^2	1.049
Largest diff. peak / hole, e Å^{-3}	2.56 / −2.59

Table 2. Selected distances (Å) and angles (deg) for $AuBr_3$(N-N) (**2**).

Au1–Br1	2.4341(18)	N1–Au1–Br1	90.6(3)
Au1–Br2	2.3959(17)	N1–Au1–Br2	178.8(3)
Au1–Br3	2.4146(19)	N1–Au1–Br3	88.3(3)
Au1–N1	2.080(11)	Br2–Au1–Br1	90.59(7)
Au51–Br51	2.4264(18)	Br2–Au1–Br3	90.45(7)
Au51–Br52	2.4029(17)	Br3–Au1–Br1	177.95(7)
Au51–Br53	2.4164(18)	N51–Au51–Br51	90.1(3)
Au51–N51	2.033(11)	N51–Au51–Br52	178.9(3)
Au1···Br52	3.5185(16)[a]	Br52–Au51–Br51	90.37(6)
Au51···Br1	3.5937(17)[a]	Br52–Au51–Br53	90.60(6)
Au1···Au51	4.408(2)[a]	Br53–Au51–Br51	178.99(6)
		N51–Au51–Br53	89.0(3)

[a] Shortest intermolecular distance.

At the final stages of refinement isotropic restraints (ISOR) were used for all non-hydrogen atoms. Despite our efforts, the internal R factor for merging equivalent intensity data (R_{int} = 0.1059) and weighted R factor of the structure refinement ($wR2$ = 0.1806) were rather large due to the poor quality of the crystals. All attempts to obtain better crystals were unsuccessful, however.

CCDC 804489 contains the supplementary crystallographic data, which can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

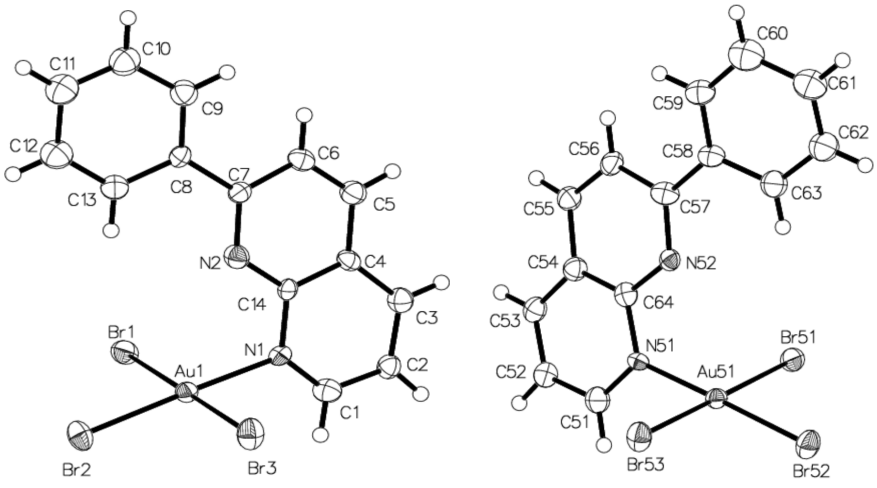

Fig. 1. ORTEP drawings of molecular structures of the two independent complex molecules in the crystal of **2** · 0.5 THF with the full atom labelling scheme used, showing displacement ellipsoids at the 50 % probability level (arbitrary spheres for the H atoms).

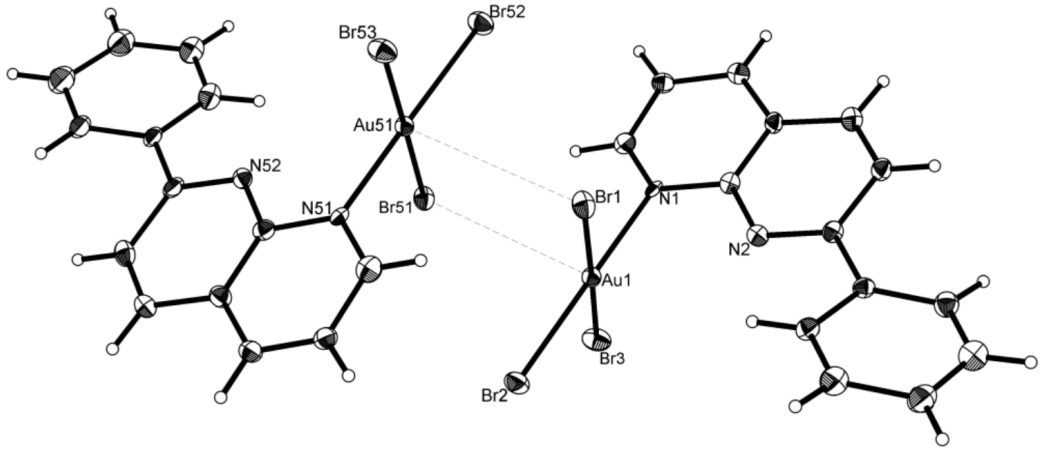

Fig. 2. ORTEP drawing of two molecules of **2** forming a dimeric unit, showing displacement ellipsoids at the 50 % probability level (arbitrary spheres for the H atoms). For the sake of clarity the THF molecule is omitted.

Results and Discussion

The crystal and molecular structure of the gold complex $AuBr_3$(N-N), **2**, was determined by X-ray diffraction studies. Table 1 gives experimental and crystallographic data. Selected bond lengths and angles are reported in Table 2.

The gold compound crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit shows (i) two symmetry-independent molecules of complex **2** and (ii) one molecule of THF solvent. Although the two gold complex molecules found in the asymmetric unit are very similar, no symmetry relationship can be found between them. Fig. 1 presents the ORTEP drawings of the molecular structures of complex **2** in the crystal of the THF solvate.

The molecular structure of molecules **2** shows three bromide ions coordinated to Au^{III} with approximately square-planar configuration at the metal atom. The bond angles at the metal center are approximately 90°, and the sum of the four angles is 360.0°. The minute displacements of the gold atoms Au1 and Au51 from their respective least-squares NBr_3 planes are 0.021(3) and 0.013(3) Å, confirming an essentially planar structure. The 1,8-naphthyridine ligand is linked to the gold center through the nitrogen atom (N^8) situated in the *unsubstituted* ring, probably for reasons of less steric interference. The bond lengths Au–Br are similar, but the Au1–Br2 and Au51–Br51 (*trans* to N) bonds are slightly shorter than the Au1–Br1/Br3 and Au51–Br51/Br53 (*cis* to N) bonds. Bond lengths Au1–N1 and Au51–N51 are

shorter by 0.335 and 0.358 Å than the average Br–Au bond length.

The angles between the least-squares planes of the naphthyridine rings N1/N2 and N51/N52 and the phenyl rings C8/C13 and C58/C63 are 21.2(5) and 22.4(5)°, respectively, indicating a somewhat less than optimum π/π conjugation between both systems. On the other hand, the dihedral angles ω between the naphthyridine plane and the corresponding $AuBr_3N$ planes are 105.9(2)° and 105.2(2)°, respectively, reflecting a sterically induced near-orthogonality.

The shortest intermolecular Au···Au distance is 4.2026(7) Å, confirming the lack of any significant interaction between the metal centers. Nevertheless, there appear to be intermolecular interactions with distances of 3.5185 and 3.5937 Å between Au1···Br51 and Au51···Br1 atoms, respectively. This interaction in the range of the sum of the van der Waals radii (3.51 Å) [16] allows for the formation of dimers in the crystal structure between two non-symmetry related gold complex molecules (Fig. 2), a feature which has been observed before in related gold(III) compounds [17].

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