



Crystal structures of seven gold(III) complexes of the form $LAuX_3$ (L = substituted pyridine, X = Cl or Br)

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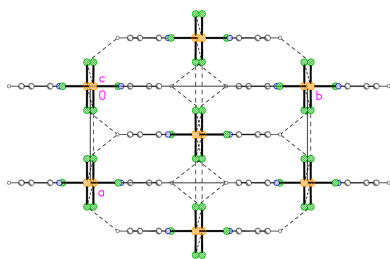
Gold complexes with amine ligands, Part 17.
Part 16: Döring & Jones (2024a).**Keywords:** crystal structure; gold; pyridine; polymorphs; twinning; halogen bonds; coinage bonds.**CCDC references:** 2145206; 2145207; 2145208; 2145212; 2145216; 2145218; 2145221; 2145222; 2145223**Supporting information:** this article has supporting information at journals.iucr.org/e

The structures of seven gold(III) halide derivatives of general formula $LAuX_3$ (L = methylpyridines or dimethylpyridines, X = Cl or Br) are presented: trichlorido(2-methylpyridine)gold(III), $[AuCl_3(C_6H_7N)]$, **1** (as two polymorphs **1a** and **1b**); tribromido(2-methylpyridine)gold(III), $[AuBr_3(C_6H_7N)]$, **2**; tribromido(3-methylpyridine)gold(III), $[AuBr_3(C_6H_7N)]$, **3**; tribromido(2,4-dimethylpyridine)gold(III), $[AuBr_3(C_7H_9N)]$, **4**; trichlorido(3,5-dimethylpyridine)gold(III), $[AuCl_3(C_7H_9N)]$, **5**; tribromido(3,5-dimethylpyridine)gold(III), $[AuBr_3(C_7H_9N)]$, **6**, and trichlorido(2,6-dimethylpyridine)gold(III), $[AuCl_3(C_7H_9N)]$, **7**. Additionally, the structure of **8**, the 1:1 adduct of **2** and **6**, $[AuBr_3(C_6H_7N)] \cdot [AuBr_3(C_7H_9N)]$, is included. All the structures crystallize solvent-free, and all have $Z' = 1$ except for **5** and **7**, which display crystallographic twofold rotation symmetry, and **4**, which has $Z' = 2$. **1a** and **2** are isotopic. The coordination geometry at the gold(III) atoms is, as expected, square-planar. Four of the crystals (**1a**, **1b**, **2** and **8**) were non-merohedral twins, and these structures were refined using the 'HKLf 5' method. The largest interplanar angles between the pyridine ring and the coordination plane are observed for those structures with a 2-methyl substituent of the pyridine ring. The Au–N bonds are consistently longer *trans* to Br (average 2.059 Å) than *trans* to Cl (average 2.036 Å). In the crystal packing, a frequent feature is the offset-stacked and approximately rectangular dimeric moiety $(Au-X)_2$, with antiparallel Au–X bonds linked by $Au \cdots X$ contacts at the vacant positions axial to the coordination plane. The dimers are connected by further secondary interactions ($Au \cdots X$ or $X \cdots X$ contacts, 'weak' C–H $\cdots X$ hydrogen bonds) to form chain, double chain ('ladder') or layer structures, and in several cases linked again in the third dimension. Only **1b** and **7** contain no offset dimers; these structures instead involve C–H $\cdots Cl$ hydrogen bonds combined with Cl $\cdots Cl$ contacts (**1b**) or Cl $\cdots \pi$ contacts (**7**). The packing patterns of seven further complexes $LAuX_3$ involving simple pyridines (taken from the Cambridge Structural Database) are compared with those of **1–8**.

1. Chemical context

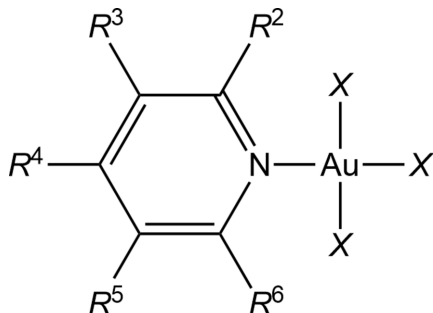
In the previous part (Döring & Jones, 2024a) of our series of publications 'Gold complexes with amine ligands', we reported the structures of four gold(I) halide complexes involving methylpyridine (picoline) and dimethylpyridine (lutidine) ligands. That publication presents much introductory material that we do not repeat here. For convenience, we have interpreted the term 'amine' liberally to include azaromatics.

In this publication we describe the structures of seven gold(III) halide derivatives of general formula $LAuX_3$ (L = methylpyridines or dimethylpyridines, X = Cl or Br). These are: trichlorido(2-methylpyridine)gold(III) **1** (as two polymorphs **1a** and **1b**); tribromido(2-methylpyridine)gold(III) **2**;



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tribromido(3-methylpyridine)gold(III) **3**; tribromido(2,4-dimethylpyridine)gold(III) **4**; trichlorido(3,5-dimethylpyridine)gold(III) **5**; tribromido(3,5-dimethylpyridine)gold(III) **6** and trichlorido(2,6-dimethylpyridine)gold(III) **7**. Additionally, we present the structure of **8**, the 1:1 adduct of **2** and **6**.



- 1** : $R^2 = \text{Me}$, $X = \text{Cl}$
2 : $R^2 = \text{Me}$, $X = \text{Br}$
3 : $R^3 = \text{Me}$, $X = \text{Br}$
4 : $R^2, R^4 = \text{Me}$, $X = \text{Br}$
5 : $R^3, R^5 = \text{Me}$, $X = \text{Cl}$
6 : $R^3, R^5 = \text{Me}$, $X = \text{Br}$
7 : $R^2, R^6 = \text{Me}$, $X = \text{Cl}$
 All other $R = \text{H}$
8 : adduct of **2** & **6**

Note added during revision: A referee commented that **8** might be referred to as a co-crystal rather than an adduct. This is certainly a reasonable suggestion in view of the IUCr definition of a co-crystal (<https://dictionary.iucr.org/Co-crystal>): ‘Solid consisting of a crystalline single-phase material composed of two or more different molecular and/or ionic compounds, generally in a stoichiometric ratio, which are neither solvates nor simple salts.’ The problem in our view is that a solid is not necessarily the same as a crystal. We would therefore prefer to say that we studied a co-crystal of the adduct **8**. The IUCr dictionary is an extremely useful document, but it is often difficult to provide watertight definitions of any given concept. For example, Bombicz (2024) recently offered reasoned criticism of the IUCr definition of ‘isostructural/isotypic’, and we supported her views in our previous paper (Döring & Jones, 2024a).

The structure of the parent compound (py)AuCl₃, Cambridge Structural Database (CSD; Groom *et al.*, 2016) refcode PYAUCL10, was presented by Adams & Strähle (1982) (‘py’ = ‘pyridine’ throughout this paper). Two other compounds with the composition (py)AuX₃ were in fact adducts of the type {[(py)₂AuX₂]⁺[AuX₄][−]·[(py)AuX₃]} [$X = \text{Cl}$, KILFIV; Bourosh *et al.* (2007); $X = \text{Br}$, WOQMEU; Peters *et al.*, 2000)]. The only related alkyipyridine structure is that of (4-Et-py)AuCl₃ (ESITIM; Hobbollahi *et al.*, 2019). Other derivatives involving ‘simple’ substituted pyridines as ligands

are the isotypic pair (4-CN-py)AuX₃ ($X = \text{Cl}$, WIRGAH or Br, WIRFUA; Mohammad-Natij *et al.*, 2013) and several complexes (3- X^1 -py)AuX₂₃ ($X^1 = \text{halogen}$, $X^2 = \text{Cl}$ or Br) (Pizzi *et al.*, 2022). The structures of this latter series and of (4-Et-py)AuCl₃ are discussed in the section *Database survey*.

2. Structural commentary

All the structures crystallize solvent-free; Z' values are 0.5 for **5** and **7**, which display crystallographic twofold symmetry (with atoms N11, C14, Au1 and Cl1 on the twofold rotation axes 0.5, y , 0.75 and 0.5, y , 0.25, respectively), 2 for **4** and 1 for all other structures. Structures **1a** and **2** are isotypic, but **5** and **6**, which also differ only in the halogen, are not. Figs. 1–9 show the molecules of these compounds in the crystal, with ellipsoids drawn at the 50% probability level. Selected bond lengths and angles are given in Tables 1–9. The molecules are numbered such that atoms X1 (and X4, where two independent molecules are present) are *trans* to the pyridinic nitrogen atoms. The numbering of X2/X3, *cis* to the pyridinic nitrogen, is chosen to make X2–Au1–N11–C12 the smallest absolute torsion angle (with appropriately altered numbering for structures with two residues). This does not apply to **5** and **7**, for which the *cis* sites are symmetry-related. The ring numbering of **6** (C12 to C16), otherwise ambiguous, is assigned by the same criterion.

The pyridine rings are as expected planar, with r.m.s. deviations of the six ring atoms between 0.002 and 0.01 Å. The coordination geometry at the central gold(III) atoms is, also as expected, square-planar; the r.m.s. deviations from the plane of Au, N and the three X atoms range from zero for **5** and **7** (by symmetry) to 0.058 Å for **3**, whereby the donor atoms alternate above and below the plane by *ca* 0.06 Å; a similar alternation is observed for the dimethylpyridine component of the adduct **8**, whereas the same molecule alone (structure **6**) has a much lower r.m.s. deviation of 0.012 Å. The angles between these two planes are 78.4 (1)° for **1a**, 84.7 (2)° for **1b**, 78.7 (2)° for **2**, 57.2 (1)° for **3**, 84.5 (1)° and 74.8 (1)° for the two molecules of **4**, 51.0 (1)° for **5**, 56.0 (1)° for **6**, 83.4 (1)° for **7** and 58.2 (2) and 84.3 (2)° for the two components of the adduct **8**, corresponding to compounds **6** and **2**. The largest angles are thus observed for those structures with a 2-methyl substituent of the pyridine ring, and presumably serve to reduce steric stress between these substituents and the X atoms *cis* to the nitrogen donor atom at Au. The gold atoms lie up to 0.15 (1) Å (for **1b**) out of the pyridine plane, but lie exactly in this plane (by symmetry) for **5** and **7**.

Bond lengths and angles may be regarded as normal. The Au–N bonds are consistently longer *trans* to Br [average (av.) of seven bonds: 2.059 Å] than *trans* to Cl (av. of four bonds: 2.036 Å), reflecting a greater *trans* influence of the bromido ligand compared to chlorido. There is no clear difference between Au–Cl bond lengths *trans* to N compared with those *cis* to N, whereas Au–Br bonds *trans* to N (av. of seven bonds: 2.395 Å) are significantly shorter than those *cis* to N (av. of fourteen bonds: 2.421 Å). The bond angles at Au are close to the ideal 90°/180°; the angles with the largest deviations for

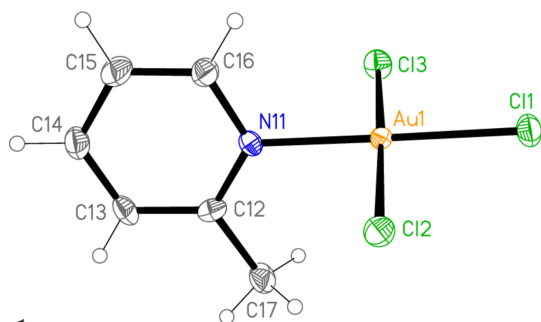


Figure 1
The molecular structure of compound **1** (polymorph **1a**) in the crystal.

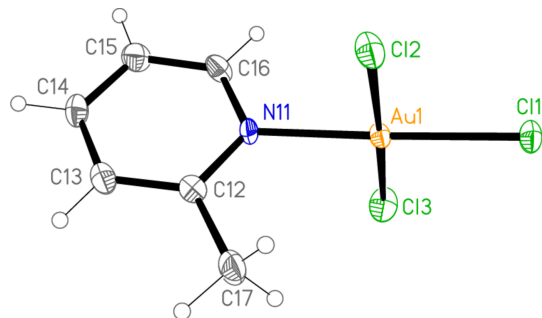


Figure 2
The molecular structure of compound **1** (polymorph **1b**) in the crystal.

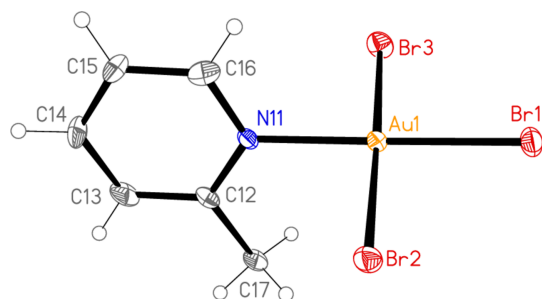


Figure 3
The molecular structure of compound **2** in the crystal.

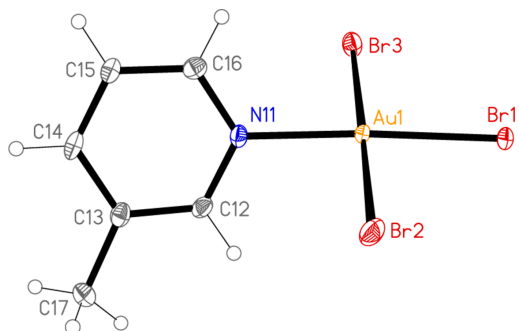


Figure 4
The molecular structure of compound **3** in the crystal.

the former are $88.25(10)^\circ$ for $N1-Au1-Br2$ of **3** and $91.17(5)^\circ$ for $Cl3-Au1-Cl1$ of **1b**, and for the latter $176.590(17)^\circ$ for $Br6-Au2-Br5$ of **4**. The C–N–C angles of the py ligands are all close to 120° (av. of eleven angles: 120.8°).

A least-squares fit of the polymorphs **1a** and **1b** gave an r.m.s. deviation of 0.08 \AA ; a similar fit of the two independent molecules of **4** (one inverted) gave a deviation of 0.16 \AA . Fits

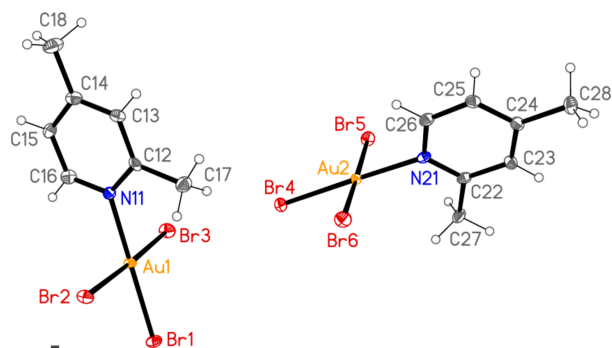


Figure 5
The molecular structure of compound **4** (with two independent molecules) in the crystal.

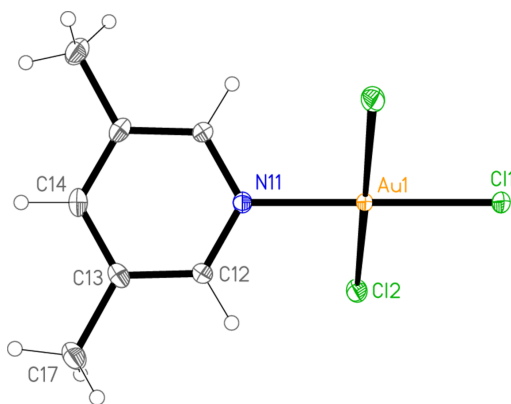


Figure 6
The molecular structure of compound **5** in the crystal. Only the asymmetric unit is numbered.

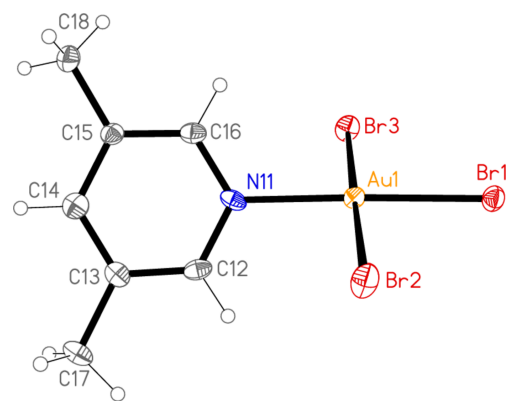


Figure 7
The molecular structure of compound **6** in the crystal.

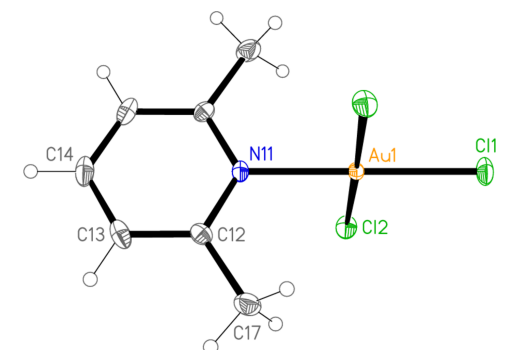


Figure 8
The molecular structure of compound **7** in the crystal. Only the asymmetric unit is numbered.

Table 1
Selected geometric parameters (Å, °) for **1a**.

Au1—N11	2.039 (4)	Au1—Cl2	2.2799 (15)
Au1—Cl3	2.2632 (15)	N11—Cl2	1.333 (7)
Au1—Cl1	2.2708 (14)	N11—Cl6	1.364 (7)
N11—Au1—Cl3	89.27 (13)	Cl3—Au1—Cl2	177.20 (5)
N11—Au1—Cl1	178.94 (13)	Cl1—Au1—Cl2	90.91 (5)
Cl3—Au1—Cl1	91.06 (6)	Cl2—N11—Cl6	121.2 (5)
N11—Au1—Cl2	88.81 (13)		
Cl3—Au1—N11—Cl2	101.8 (4)	Cl3—Au1—N11—Cl6	−80.4 (4)
Cl2—Au1—N11—Cl2	−76.2 (4)	Cl2—Au1—N11—Cl6	101.6 (4)

Table 2
Selected geometric parameters (Å, °) for **1b**.

Au1—N11	2.030 (4)	Au1—Cl2	2.2766 (12)
Au1—Cl3	2.2652 (14)	N11—Cl6	1.347 (6)
Au1—Cl1	2.2688 (13)	N11—Cl2	1.354 (7)
N11—Au1—Cl3	89.65 (14)	Cl3—Au1—Cl2	177.79 (5)
N11—Au1—Cl1	178.32 (13)	Cl1—Au1—Cl2	90.90 (5)
Cl3—Au1—Cl1	91.17 (5)	Cl6—N11—Cl2	120.1 (5)
N11—Au1—Cl2	88.27 (13)		
Cl3—Au1—N11—Cl6	−86.0 (4)	Cl3—Au1—N11—Cl2	98.2 (4)
Cl2—Au1—N11—Cl6	93.3 (4)	Cl2—Au1—N11—Cl2	−82.5 (4)

Table 3
Selected geometric parameters (Å, °) for **2**.

Au1—N11	2.050 (5)	Au1—Br2	2.4220 (8)
Au1—Br1	2.3996 (7)	N11—Cl6	1.349 (7)
Au1—Br3	2.4085 (8)	N11—Cl2	1.359 (8)
N11—Au1—Br1	178.93 (15)	Br1—Au1—Br2	90.88 (3)
N11—Au1—Br3	89.24 (16)	Br3—Au1—Br2	177.16 (3)
Br1—Au1—Br3	90.84 (3)	Cl6—N11—Cl2	120.3 (6)
N11—Au1—Br2	89.08 (16)		
Br3—Au1—N11—Cl6	−80.7 (5)	Br3—Au1—N11—Cl2	101.2 (5)
Br2—Au1—N11—Cl6	101.6 (5)	Br2—Au1—N11—Cl2	−76.5 (5)

of molecules **2** and **6** (the latter inverted) to the same molecules of the adduct **8** gave r.m.s. deviations of 0.091 and 0.061 Å, respectively. More informative figures are however obtained by fitting only the pyridine ligands, which are closely similar; the differences associated with the AuX₃ moieties are

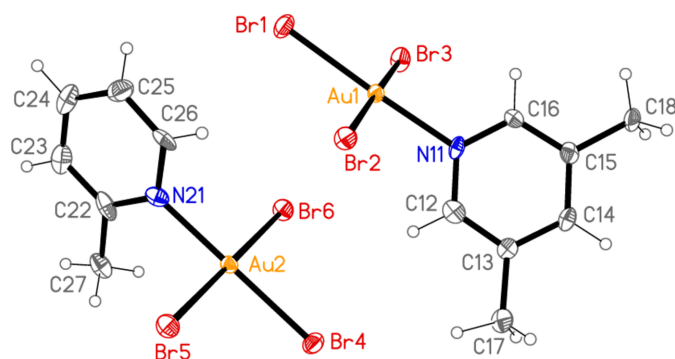


Figure 9
The molecular structures of compound **8** (an adduct of **2** and **6**) in the crystal.

Table 4
Selected geometric parameters (Å, °) for **3**.

Au1—N11	2.062 (4)	Au1—Br3	2.4276 (5)
Au1—Br1	2.4009 (5)	N11—Cl6	1.341 (6)
Au1—Br2	2.4225 (5)	N11—Cl2	1.346 (6)
N11—Au1—Br1	176.62 (10)	Br1—Au1—Br3	90.653 (17)
N11—Au1—Br2	88.25 (10)	Br2—Au1—Br3	176.494 (17)
Br1—Au1—Br2	90.649 (17)	Cl6—N11—Cl2	120.3 (4)
N11—Au1—Br3	90.63 (10)		
Br2—Au1—N11—Cl6	120.5 (3)	Br2—Au1—N11—Cl2	−58.4 (3)
Br3—Au1—N11—Cl6	−56.1 (3)	Br3—Au1—N11—Cl2	124.9 (3)

Table 5
Selected geometric parameters (Å, °) for **4**.

Au1—N11	2.062 (3)	Au2—N21	2.054 (4)
Au1—Br1	2.3998 (4)	Au2—Br4	2.3963 (4)
Au1—Br3	2.4070 (5)	Au2—Br6	2.4187 (5)
Au1—Br2	2.4235 (4)	Au2—Br5	2.4266 (5)
N11—Cl6	1.336 (5)	N21—C22	1.346 (5)
N11—Cl2	1.350 (5)	N21—C26	1.348 (5)
N11—Au1—Br1	179.86 (11)	N21—Au2—Br4	178.91 (10)
N11—Au1—Br3	88.97 (10)	N21—Au2—Br6	88.46 (10)
Br1—Au1—Br3	90.901 (16)	Br4—Au2—Br6	90.810 (16)
N11—Au1—Br2	89.16 (10)	N21—Au2—Br5	90.10 (10)
Br1—Au1—Br2	90.974 (15)	Br4—Au2—Br5	90.672 (16)
Br3—Au1—Br2	177.518 (17)	Br6—Au2—Br5	176.590 (17)
C16—N11—Cl2	120.5 (4)	C22—N21—C26	120.8 (4)
Br3—Au1—N11—Cl6	84.7 (3)	Br6—Au2—N21—C22	106.4 (3)
Br2—Au1—N11—Cl6	−93.7 (3)	Br5—Au2—N21—C22	−76.7 (3)
Br3—Au1—N11—Cl2	−97.3 (3)	Br6—Au2—N21—C26	−72.5 (3)
Br2—Au1—N11—Cl2	84.3 (3)	Br5—Au2—N21—C26	104.4 (3)

Table 6
Selected geometric parameters (Å, °) for **5**.

Au1—N11	2.037 (3)	Au1—Cl2	2.2867 (6)
Au1—Cl1	2.2716 (8)	N11—Cl2	1.352 (3)
N11—Au1—Cl1	180.0	Cl2—Au1—Cl2 ⁱ	179.56 (3)
N11—Au1—Cl2	89.779 (14)	Cl2—N11—Cl2 ⁱ	121.0 (3)
Cl1—Au1—Cl2	90.221 (14)		
Cl2—Au1—N11—Cl2	51.15 (11)	Cl2—Au1—N11—Cl2 ⁱ	−128.85 (11)

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

Table 7
Selected geometric parameters (Å, °) for **6**.

Au1—N11	2.078 (4)	Au1—Br3	2.4295 (4)
Au1—Br1	2.3892 (5)	N11—Cl6	1.344 (6)
Au1—Br2	2.4167 (5)		
N11—Au1—Br1	178.39 (10)	Br1—Au1—Br3	89.674 (17)
N11—Au1—Br2	90.03 (10)	Br2—Au1—Br3	179.045 (17)
Br1—Au1—Br2	89.437 (17)	Cl6—N11—Cl2	121.8 (4)
N11—Au1—Br3	90.85 (10)		
Br2—Au1—N11—Cl6	124.0 (3)	Br2—Au1—N11—Cl2	−55.8 (3)
Br3—Au1—N11—Cl6	−56.3 (3)	Br3—Au1—N11—Cl2	123.9 (3)

then shown more clearly. For **1a/1b**, the atoms Cl2 and Cl3 differ in position by 0.26 and 0.20 Å respectively (Fig. 10). For **4**, the gold atoms lie on opposite sides of the pyridine plane, and this, coupled with the 10° difference in the interplanar

Table 8
Selected geometric parameters (Å, °) for **7**.

Au1–N11	2.036 (2)	Au1–Cl2	2.2811 (5)
Au1–Cl1	2.2648 (7)	N11–Cl2	1.360 (2)
N11–Au1–Cl1	180.0	Cl2–Au1–Cl2 ⁱ	178.75 (2)
N11–Au1–Cl2	89.375 (12)	Cl2 ⁱ –N11–Cl2	121.7 (2)
Cl1–Au1–Cl2	90.625 (12)		
Cl2–Au1–N11–Cl2 ⁱ	–92.76 (10)	Cl2–Au1–N11–Cl2	87.24 (10)

Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.

Table 9
Selected geometric parameters (Å, °) for **8**.

Au1–N11	2.053 (8)	Au2–Br5	2.4136 (9)
Au1–Br1	2.3922 (11)	Au2–Br6	2.4253 (10)
Au1–Br3	2.4162 (9)	N11–Cl2	1.347 (11)
Au1–Br2	2.4306 (10)	N11–Cl6	1.360 (10)
Au2–N21	2.056 (8)	N21–C26	1.348 (11)
Au2–Br4	2.3901 (11)	N21–C22	1.360 (11)
N11–Au1–Br1	177.6 (2)	N21–Au2–Br5	89.90 (19)
N11–Au1–Br3	90.3 (2)	Br4–Au2–Br5	90.14 (4)
Br1–Au1–Br3	90.02 (4)	N21–Au2–Br6	89.95 (19)
N11–Au1–Br2	89.0 (2)	Br4–Au2–Br6	90.01 (4)
Br1–Au1–Br2	90.84 (4)	Br5–Au2–Br6	179.59 (4)
Br3–Au1–Br2	176.66 (4)	Cl2–N11–Cl6	120.2 (9)
N21–Au2–Br4	179.8 (2)	C26–N21–C22	120.6 (9)
Br3–Au1–N11–Cl2	–121.6 (6)	Br5–Au2–N21–C26	96.6 (6)
Br2–Au1–N11–Cl2	55.2 (6)	Br6–Au2–N21–C26	–83.8 (6)
Br3–Au1–N11–Cl6	60.5 (6)	Br5–Au2–N21–C22	–86.0 (7)
Br2–Au1–N11–Cl6	–122.7 (6)	Br6–Au2–N21–C22	93.7 (7)

angle, leads to significant differences in the positions of the bromine atoms (0.39, 0.50, 0.51 Å, respectively for Br1–3; Fig. 11). A similar effect, although the interplanar angles are almost equal, is seen for the fit of **1b** with its counterpart in the adduct **8** (deviations 0.50, 0.43, 0.40 Å; Fig. 12), whereas the largest difference for the fit of **6** with its counterpart in **8** is for Br1 (0.22 Å; Fig. 13).

3. Supramolecular features

Hydrogen bonds of the type C–H...X for all structures are given in Tables 10–18. These include several borderline cases that are not discussed explicitly. For all packing diagrams, the

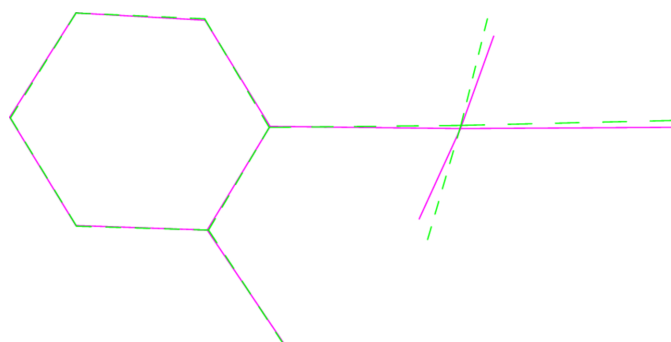


Figure 10
A least-squares fit of the pyridinic ligands of **1a** and **1b** (excluding H atoms). **1a** is the dotted molecule.

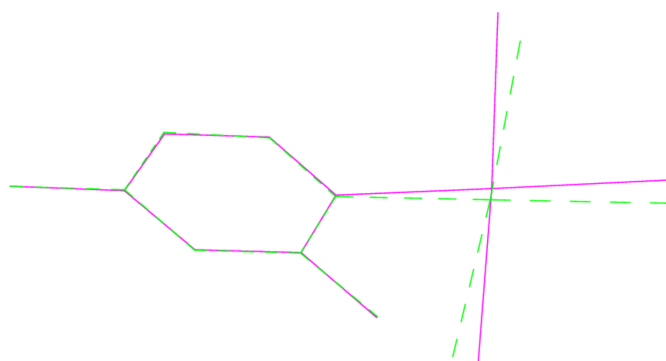


Figure 11
A least-squares fit of the pyridinic ligands of both molecules of **4** (excluding H atoms). Molecule 1 (centred on Au1) is dotted.

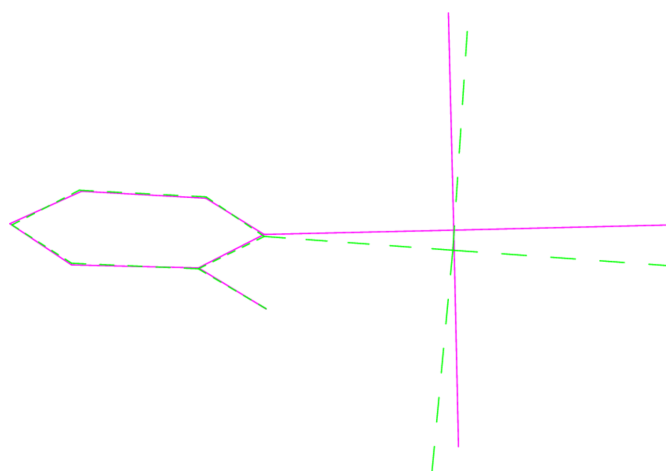


Figure 12
A least-squares fit of the pyridinic ligands of **1b** and its counterpart in the adduct **8** (excluding H atoms). **1b** is the dotted molecule.

labelling indicates the asymmetric unit, and hydrogen atoms not involved in secondary contacts are omitted for clarity. The choice of ‘important’ interactions and their hierarchy is necessarily subjective, at least to some extent; diagrams with a

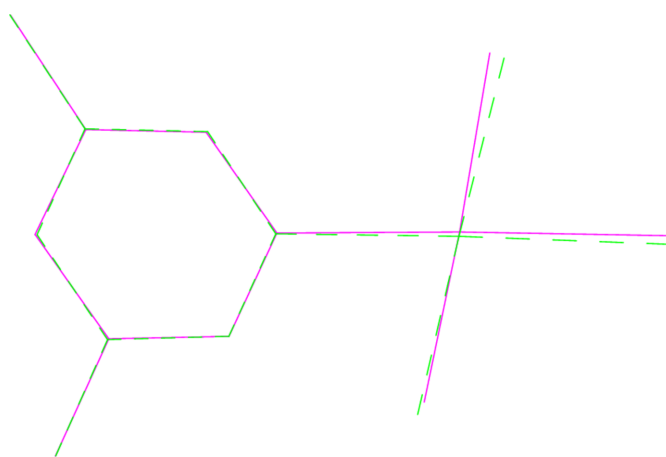


Figure 13
A least-squares fit of the pyridinic ligands of **6** and its counterpart in the adduct **8** (excluding H atoms). **6** is the dotted molecule.

Table 10
Hydrogen-bond geometry (Å, °) for **1a**.

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C17—H17 <i>B</i> ···Cl1 ⁱ	0.98	2.96	3.888 (6)	159
C14—H14···Cl2 ⁱⁱ	0.95	2.93	3.538 (6)	123
C16—H16···Cl2 ⁱⁱⁱ	0.95	2.75	3.553 (6)	142
C17—H17 <i>C</i> ···Cl2	0.98	2.90	3.596 (6)	129

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z + 2$.

Table 11
Hydrogen-bond geometry (Å, °) for **1b**.

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C13—H13···Cl1 ⁱ	0.95	2.79	3.683 (6)	157
C15—H15···Cl1 ⁱⁱ	0.95	2.88	3.527 (6)	126
C17—H17 <i>C</i> ···Cl1 ⁱ	0.98	2.86	3.798 (6)	160
C16—H16···Cl2 ⁱⁱⁱ	0.95	2.70	3.610 (6)	162

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x, -y + 1, -z$.

Table 12
Hydrogen-bond geometry (Å, °) for **2**.

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C14—H14···Br1 ⁱ	0.95	3.09	3.754 (7)	129
C17—H17 <i>A</i> ···Br1 ⁱⁱ	0.98	3.05	3.972 (7)	156
C17—H17 <i>B</i> ···Br1 ⁱⁱⁱ	0.98	3.06	3.982 (6)	157
C14—H14···Br2 ^{iv}	0.95	3.04	3.636 (7)	122
C16—H16···Br2 ^v	0.95	2.86	3.683 (7)	146
C17—H17 <i>C</i> ···Br2	0.98	2.96	3.690 (7)	132

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $x, y, z - 1$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $-x + 1, -y + 1, -z + 2$.

Table 13
Hydrogen-bond geometry (Å, °) for **3**.

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C15—H15···Br1 ⁱ	0.95	2.97	3.905 (5)	168
C16—H16···Br1 ⁱⁱ	0.95	2.86	3.721 (5)	151
C12—H12···Br2 ⁱⁱⁱ	0.95	2.88	3.684 (4)	144
C14—H14···Br3 ^{iv}	0.95	3.08	3.880 (5)	143
C17—H17 <i>B</i> ···Br3 ^{iv}	0.98	3.06	3.984 (5)	159

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, -y, -z + 1$.

Table 14
Hydrogen-bond geometry (Å, °) for **4**.

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C16—H16···Br2 ⁱ	0.95	2.86	3.755 (5)	158
C17—H17 <i>C</i> ···Br4	0.98	2.89	3.861 (5)	171
C23—H23···Br4 ⁱⁱ	0.95	2.95	3.765 (4)	145
C25—H25···Br2 ⁱⁱⁱ	0.95	2.92	3.851 (4)	166
C26—H26···Br5 ^{iv}	0.95	2.98	3.890 (4)	161
C27—H27 <i>B</i> ···Br3 ⁱⁱ	0.98	3.07	3.855 (4)	138
C27—H27 <i>C</i> ···Br5	0.98	3.01	3.647 (4)	124

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $x, -y + \frac{3}{2}, z + \frac{3}{2}$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x, -y + 1, -z + 1$.

Table 15
Hydrogen-bond geometry (Å, °) for **5**.

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C12—H12···Cl1 ⁱⁱ	0.95	2.67	3.564 (2)	158
C14—H14···Cl2 ⁱⁱⁱ	0.95	2.87	3.659 (3)	142
C14—H14···Cl2 ^{iv}	0.95	2.87	3.659 (3)	142

Symmetry codes: (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

Table 16
Hydrogen-bond geometry (Å, °) for **6**.

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C16—H16···Br1 ⁱ	0.95	2.91	3.792 (4)	154
C17—H17 <i>C</i> ···Br1 ⁱⁱ	0.98	2.87	3.749 (5)	149
C18—H18 <i>A</i> ···Br1 ⁱ	0.98	2.89	3.784 (5)	151
C18—H18 <i>C</i> ···Br3 ⁱⁱⁱ	0.98	2.93	3.902 (5)	174
C14—H14···Br2 ^{iv}	0.95	3.02	3.826 (5)	144

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x, y, z + 1$; (iii) $-x, -y + 1, -z + 2$; (iv) $-x + 1, -y + 1, -z + 2$.

Table 17
Hydrogen-bond geometry (Å, °) for **7**.

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C17—H17 <i>C</i> ···Cl1 ⁱⁱ	0.98	2.87	3.701 (2)	144
C14—H14···Cl1 ⁱⁱⁱ	0.95	2.67	3.621 (3)	180

Symmetry codes: (ii) $-x + 1, -y, -z$; (iii) $x, y + 1, z$.

Table 18
Hydrogen-bond geometry (Å, °) for **8**.

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C18—H18 <i>C</i> ···Br3 ⁱ	0.98	3.05	3.892 (10)	145
C23—H23···Br4 ⁱⁱ	0.95	3.01	3.815 (10)	143
C17—H17 <i>C</i> ···Br6 ⁱ	0.98	2.90	3.792 (10)	152
C16—H16···Br5 ⁱⁱⁱ	0.95	3.06	4.007 (9)	172
C25—H25···Br1 ^{iv}	0.95	3.06	3.721 (10)	128
C26—H26···Br2	0.95	2.94	3.835 (10)	159

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$; (iii) $x, y, z + 1$; (iv) $-x, -y, -z + 1$.

small number of heavy-atom contacts are easier to interpret than those involving a larger number of hydrogen bonds, and this is especially true for H···Br contacts, which are probably weaker than H···Cl. Primes (',') indicate symmetry-equivalent atoms; operators are not given in full each time. A summary of the packing features is given in Table 19.

Before discussing the packing of **1–8** in detail, it is useful to look back on the packing of (py)AuCl₃ (Adams & Strähle, 1982; space group *C2/c*, *Z* = 8), to see what types of secondary interaction can arise. Short non-bonded contacts were observed between the gold atom and two chlorine atoms, positioned axially to the main coordination plane in such a way as to complete a highly stretched octahedron at the gold atom (Au···Cl 3.636 and 3.648 Å, Cl···Au···Cl 173.0°; operators $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$ and $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$). This leads to ladder-like double chains of residues (Fig. 14), parallel to the *b* axis, in which the molecules display offset stacking of the AuX₃ groups; one Au—Cl bond of each molecule (the rungs of the ladder) shares two Au···Cl contacts with anti-parallel Cl—Au bonds of each neighbouring molecule (the side rails of the ladder). The (Au—X)₂ quadrilaterals, approximately rectangular and with side lengths corresponding to the Au—Cl bond length and the Au···Cl contact distance, are a recurring feature in the structures discussed here. Offset stacking of this type is a common feature in AuX₃ complexes, and we have observed it *e.g.* in four modifications of (tetrahydrothiophene)AuCl₃ (Upmann *et al.*, 2017). In general, any suitable donor atoms can occupy these two contact sites. It might be argued that such contacts are merely connected with the steric ease of approach to the two sides of

Table 19
Summary of packing features.

Compound	No. of axial Au...X contacts	Offset-stacked dimers [(Au-X) ₂ quadrilaterals]	Connected to form ... ^b	Further linkages ^b
(py)AuCl (Adams & Strähle, 1982)	2	yes	double chain (ladder) <i>via</i> edge-linked quadrilaterals	
1a and 2 (isotypic)	1	yes	double chain <i>via</i> X...X contacts	
1b	0	no	double chain <i>via</i> Cl...Cl and H...Cl contacts	
3	2	yes	layer <i>via</i> Br...Br contacts	layers connected <i>via</i> Br...Br contacts
4 (both molecules)	1	yes	double chain <i>via</i> Br...Br contacts (analogous to 1a and 2)	layers connected <i>via</i> Br...Br contacts
5	2	yes	chain <i>via</i> apex-linked quadrilaterals	connected to form layers <i>via</i> Cl...Cl contacts
6	1	yes	double chain <i>via</i> Br...Br contacts (analogous to 1a and 2)	connected to form double layer <i>via</i> Br...Br contacts
7	0	no	layer <i>via</i> H...Cl and Cl...π contacts	
8	Au1 2, Au2 0	Au1 yes, Au2 no	layer <i>via</i> Br...Br contacts	layers connected <i>via</i> Br...Br contacts
ESITIM (Hobbollahi <i>et al.</i> , 2019) ^a	2	no	layer structure with linked tetrameric rings	
WEFQAD (Pizzi <i>et al.</i> , 2022) ^a	2	yes	ladder structure	ladders connected <i>via</i> Br...Cl contacts
WEFQEH (Pizzi <i>et al.</i> , 2022) ^a	2	no	layer structure analogous to ESITIM	layers connected <i>via</i> F...F contacts
WEFQIL (Pizzi <i>et al.</i> , 2022) ^a	2	yes	chain <i>via</i> apex-linked quadrilaterals	connected to form layers <i>via</i> Cl...Cl _{py} contacts
WEFOOR (Pizzi <i>et al.</i> , 2022) ^a	2	yes	ladder structure	connected to form layers <i>via</i> I...Cl contacts.
WEFRAE (Pizzi <i>et al.</i> , 2022) ^a	2	yes	chain <i>via</i> apex-linked quadrilaterals	connected to form layers <i>via</i> Br...Br contacts

Notes: (a) Refcodes refer to structures whose packing is discussed in the section *Database survey*; (b) these columns do not necessarily present an exhaustive list; see text for further details.

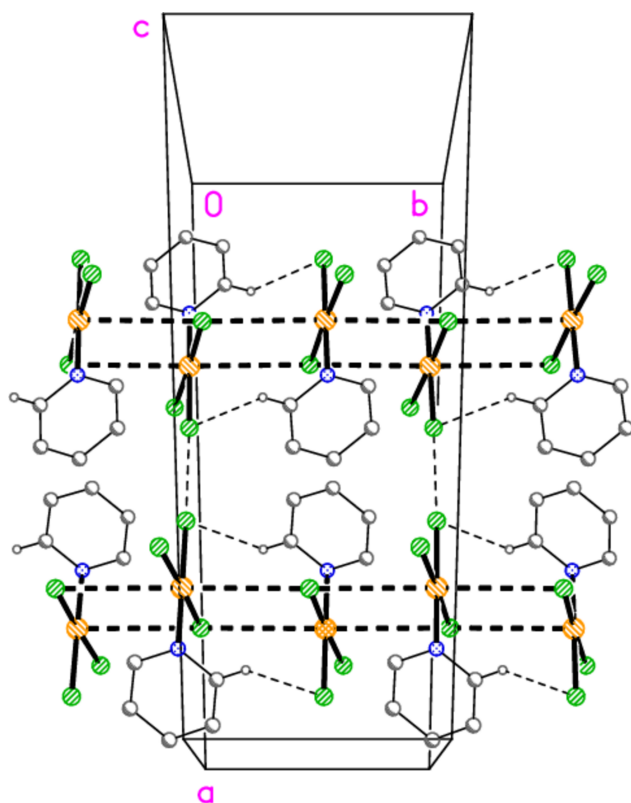
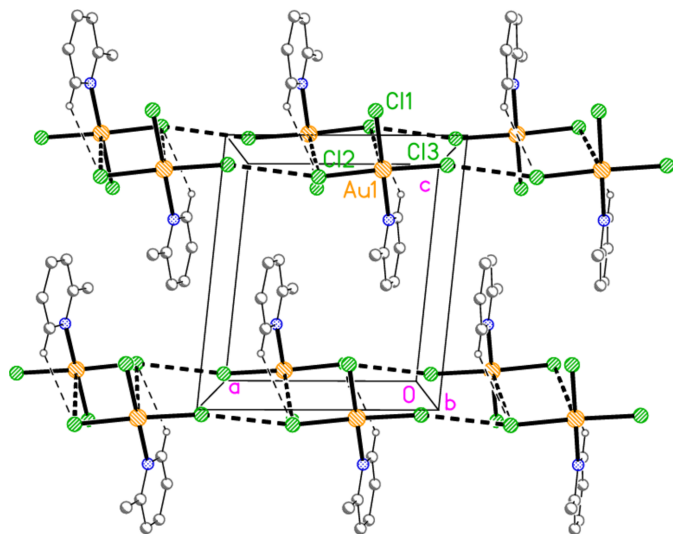


Figure 14
The packing of (py)AuCl₃ (Adams & Strähle, 1982), showing two adjacent ladder-like double chains parallel to the *b* axis at (*x*, *z*) = (0.25, 0) and (0.75, 0.5). The view direction is approximately parallel to the *c* axis (but rotated slightly to reduce overlap). Thick dashed lines indicate Au...Cl contacts; thin dashed lines indicate ‘weak’ H...Cl hydrogen bonds or short Cl...Cl contacts. Atomic coordinates were taken from the database (refcode PYAUCL10); hydrogen-atom positions were calculated using the HADD option of XP (Bruker, 1998). Colour codes for this Figure and for Figs. 29–34 are the same as for those of **1–8** (C and H black, N dark blue, Au yellow, Cl green, Br brick-red), but we do not number the atoms in these Figures because the database numbering is not consistent *e.g.* for *cis* and *trans* halogen atoms.

the coordination plane; this has also been argued for short contacts to the linearly coordinated gold atom of gold(I) complexes, although H...Au hydrogen bonding in such systems is reasonably well established (Schmidbaur, 2019; Schmidbaur *et al.*, 2014). However, recent studies and calculations (Daolio *et al.*, 2021; Pizzi *et al.*, 2022) have indicated that there is a π-hole at the gold atom, and that there is thus a definite attractive interaction, a ‘coinage bond’, between the gold atom and the additional donor(s) (see below).

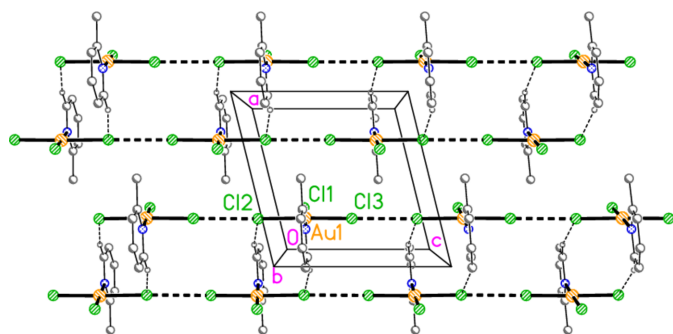
At the time of publication of the (py)AuCl₃ structure, more than 40 years ago (the data were probably recorded in the late 1970s), the main interest in crystal structure determinations generally centred on the molecule being studied, whereas intermolecular contacts were often neglected. The analysis of the Au...Cl contacts in (py)AuCl₃ constituted a welcome exception. However, the structure contains other secondary contacts that were not mentioned, probably because at the time such contacts were not regarded as significant. First, there is a short Cl...Cl contact of 3.462 Å connecting the ‘ladders’. Such formally non-bonding contacts between halogen atoms have been the subject of considerable interest for some time and are usually termed ‘halogen bonds’. For C–X...X–C systems, they are considered to involve a small region of positive charge in the extension of the C–X bond vectors beyond the atom X, often leading to one C–X...X angle of *ca* 90° and one of *ca* 180° (see *e.g.* Metrangolo *et al.*, 2008, or Cavallo *et al.*, 2016, for review articles); they are quite common for Au–X systems, but we are not aware of any systematic and/or theoretical study of X...X contacts in these systems. We have drawn attention to X...X contacts in various tetrahalogenidoaurate(III) salts (*e.g.* Döring & Jones, 2016) and in LAuX₃ complexes (*e.g.* Döring & Jones, 2024b), and recently presented a short database survey of the latter (Döring & Jones, 2023). Secondly, there are short contacts of


Figure 15

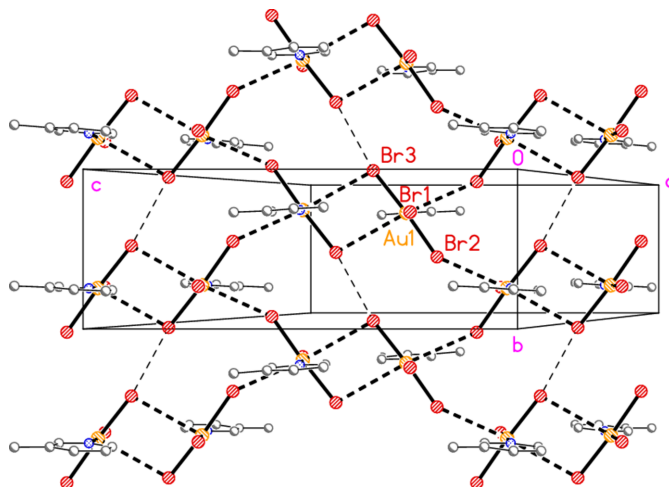
Packing diagram of compound **1**, polymorph **1a**, viewed parallel to the *b* axis in the region $y \approx 0.5$. Dashed bonds indicate Au···Cl or Cl···Cl contacts (thick) or H···Cl hydrogen bonds (thin).

the type C—H···Cl that are now regarded as hydrogen bonds and are, somewhat misleadingly, often termed ‘weak’ hydrogen bonds. These were not mentioned in the 1982 publication, and indeed no hydrogen atoms were included in the refinement, which was not unusual at the time for heavy-atom structures. We used the program *XP* (Bruker, 1998) to calculate the hydrogen-atom positions, and established that there are three short H···Cl contacts, one as short as 2.79 Å; this connects neighbouring molecules in the ladders. Two further such contacts (2.85 and 2.86 Å) connect the ladders; these are omitted from Fig. 14 for clarity.

The packing diagram of compound **1a** is shown in Fig. 15. The molecules are linked to form inversion-symmetric dimers (operator $1 - x, 1 - y, 2 - z$) in an offset packing pattern, with $\text{Au1} \cdots \text{Cl2}' = 3.441$ (2) Å; reinforcement is provided by the shortest hydrogen bond $\text{H16} \cdots \text{Cl2}'$. The dimers are in turn linked by a short contact $\text{Cl2} \cdots \text{Cl3}(1 + x, y, z) = 3.239$ (2) Å to form double chains parallel to the *a* axis. The angles $\text{Au1} - \text{Cl2} \cdots \text{Cl3}'$ and $\text{Au1} - \text{Cl3} \cdots \text{Cl2}'$ are 161.09 (6) and


Figure 16

Packing diagram of compound **1**, polymorph **1b**, viewed parallel to the *b* axis in the region $y \approx 0.5$. Dashed bonds indicate Cl···Cl contacts (thick) or H···Cl hydrogen bonds (thin).


Figure 17

Packing diagram of compound **3**, viewed perpendicular to the *bc* plane in the region $x \approx 0.25$. Dashed bonds indicate Au···Br contacts (thick) or Br3···Br3 contacts (thin).

162.30 (7)°, respectively. There are no other Cl···Cl contacts < 3.8 Å. In the packing of compound **2** (isotypic to **1a**) the corresponding dimensions are $\text{Au1} \cdots \text{Br2}' = 3.5654$ (8), $\text{Br2} \cdots \text{Br3} = 3.3840$ (9) Å, $\text{Au1} - \text{Br2} \cdots \text{Br3}' = 164.38$ (3), $\text{Au1} - \text{Br3} \cdots \text{Br2}' = 159.34$ (3)°. The second polymorph **1b** has no Au···Cl contact shorter than 3.833 (2) Å for $\text{Au1} \cdots \text{Cl2}(-x, 1 - y, -z)$, but has an even shorter Cl···Cl contact: $\text{Cl2} \cdots \text{Cl3}(x, y, -1 + z) = 3.164$ (2) Å. This combines with the shortest H···Cl hydrogen bond, again $\text{H16} \cdots \text{Cl2}$, to form double chains of molecules parallel to the *a* axis (Fig. 16), with $\text{Au1} - \text{Cl2} \cdots \text{Cl3}' = 172.65$ (7)° and $\text{Au1} - \text{Cl3} \cdots \text{Cl2}' = 174.55$ (8)°. The double chains are linked in the *b* direction by the hydrogen bond $\text{H13} \cdots \text{Cl1}$. It is notable throughout this series of structures that the *cis* (to the pyridine ligands) halogen atoms *X2* and *X3* (or *X5* and *X6*) tend to be involved in the main packing features, whereas the *trans* halogen atom *X1* (or *X4*) often provides the additional linkages.

The packing of compound **3** consists of layers parallel to the *bc* plane (Fig. 17) at $x \approx 0.25$ and 0.75, in which the two contacts $\text{Au1} \cdots \text{Br2}(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z) = 3.4688$ (5) Å and $\text{Au1} \cdots \text{Br3}(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z) = 3.6535$ (5) Å complete a stretched octahedron at the gold atom [angles $\text{Br2}' \cdots \text{Au1} \cdots \text{Br3}' = 173.91$ (1)°, $\text{Au1} - \text{Br2} \cdots \text{Au1}' = 148.42$ (2)°]. The Au1···Br3 contacts generate an offset-stacked dimer, but this stacking is not further extended. The contact $\text{Br3} \cdots \text{Br3}(\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z) = 3.5256$ (9) Å completes the layer, with $\text{Au1} - \text{Br3} \cdots \text{Br3}' = 170.31$ (3)°. The two shortest H···Br contacts also lie within this layer, but are omitted from Fig. 17 for clarity. The layers are linked by the $\text{Br1} \cdots \text{Br1}(-x, y, \frac{1}{2} + z)$ contact of 3.4531 (9) Å, with $\text{Au1} - \text{Br1} \cdots \text{Br1}' = 174.62$ (3) Å, and by stacking of the pyridine rings [intercentroid distances 3.657 (2) and 3.619 (2) Å, slippage 1.28 and 1.38 Å, operators $1 - x, -y, 1 - z$ and $1 - x, 1 - y, 1 - z$ respectively] (Fig. 18). No other structure presented here has an intercentroid distance between the rings < 3.70 Å.

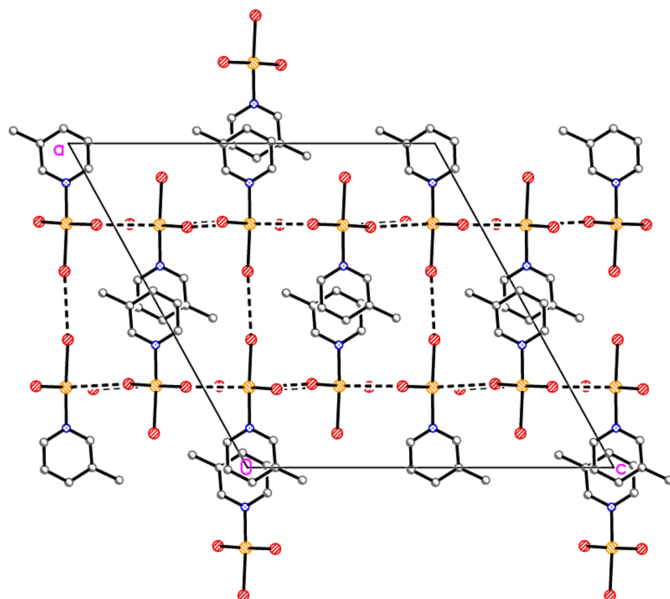


Figure 18
Packing diagram of compound **3**, projected parallel to the *b* axis, showing the linking of the layers of Fig. 17 by the Br1...Br1 contacts (thick dashed lines, vertical).

The packing of compound **4** is closely related to that of **1a**. Each independent molecule forms double chains parallel to the *a* axis that are topologically analogous to those of **1a**, with

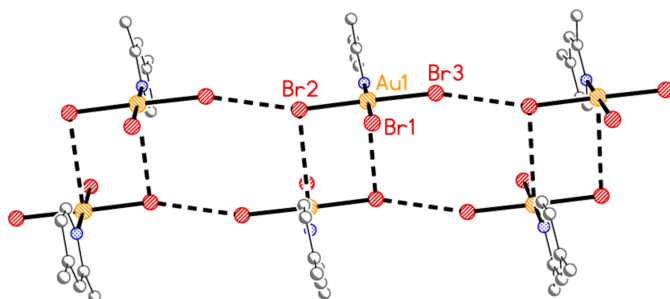


Figure 19
A double chain of molecules **1** for compound **4**, with view direction parallel to the *b* axis. Dashed lines indicate Au...Br and Br...Br contacts.

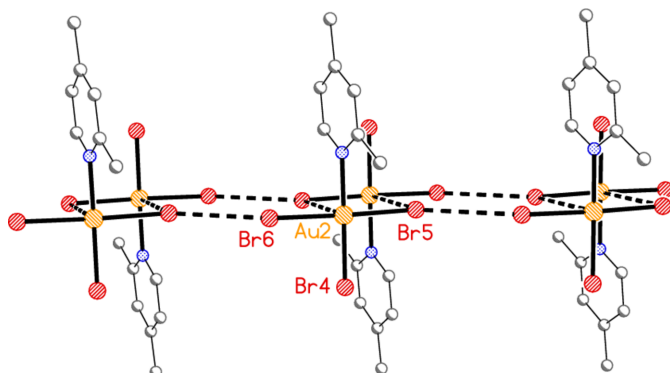


Figure 20
A double chain of molecules **2** for compound **4**, with view direction parallel to the *b* axis. Dashed lines indicate Au...Br and Br...Br contacts.

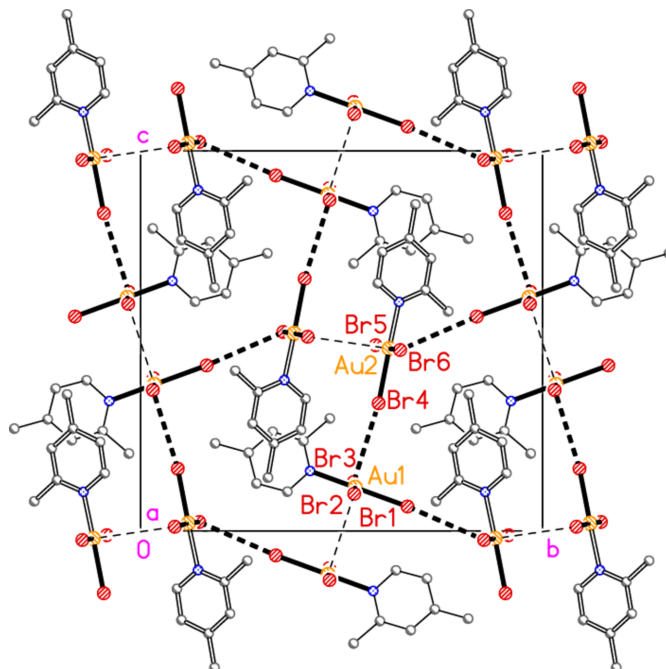


Figure 21
Projection of the structure of compound **4** parallel to the *a* axis. Molecules **2** are indicated by the thicker bonds of the rings. Thick dashed lines indicate Br...Br contacts between the double chains of molecule **1** and **2** (in the regions $y \approx 0.5$, $z \approx 0$ and $y \approx 0.5$, $z \approx 0.5$ respectively, and in regions related to these by symmetry). Thin dashed lines are contacts within the chains, as seen in the previous two figures.

dimers arising from antiparallel (Au—Br)₂ contacts and further linked by Br...Br contacts; dimensions (Å and °) are Au1...Br2(1 - *x*, 1 - *y*, -*z*) = 3.6606 (5), Br2...Br3(1 + *x*, *y*, *z*) = 3.3117 (6), Au—Br2...Br3' = 164.67 (2), Au1—Br3...Br2' = 165.45 (2) for the first molecule (Fig. 19) and Au2...Br5(-*x*, 1 - *y*, 1 - *z*) = 3.8328 (5), Br5...Br6(-1 + *x*, *y*, *z*) = 3.5191 (6), Au2—Br5...Br6' = 147.93 (2), Au2—Br6...Br5' = 151.00 (2) for the second molecule (Fig. 20). It is

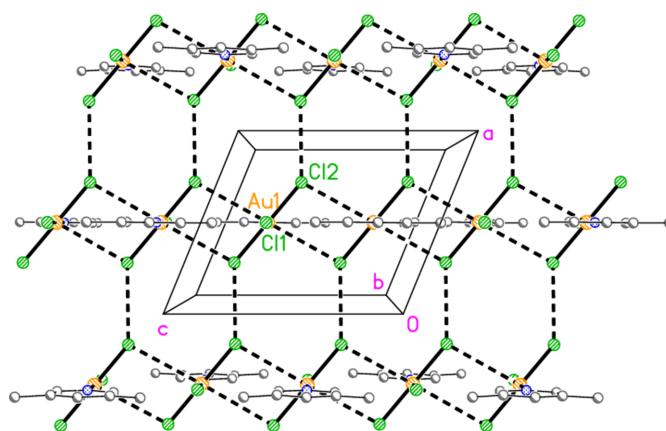
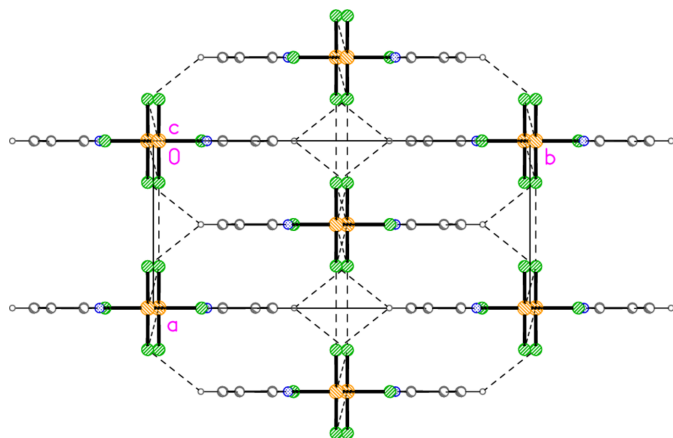


Figure 22
The layer structure of compound **5** viewed parallel to the *b* axis. Dashed lines indicate Au...Cl and Cl...Cl interactions. The Au coordination planes are seen edge-on, so that Au1 obscures Cl1 or vice versa.

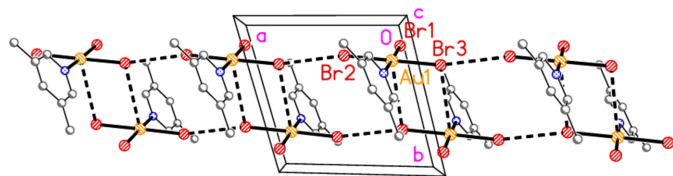

Figure 23

Projection of the structure of compound **5** viewed perpendicular to the *ab* plane. The dashed lines connecting the layers (see Fig. 22) are the three-centre hydrogen bonds $\text{H14} \cdots \text{Cl2}$ (with two symmetry-equivalent Cl2 atoms).

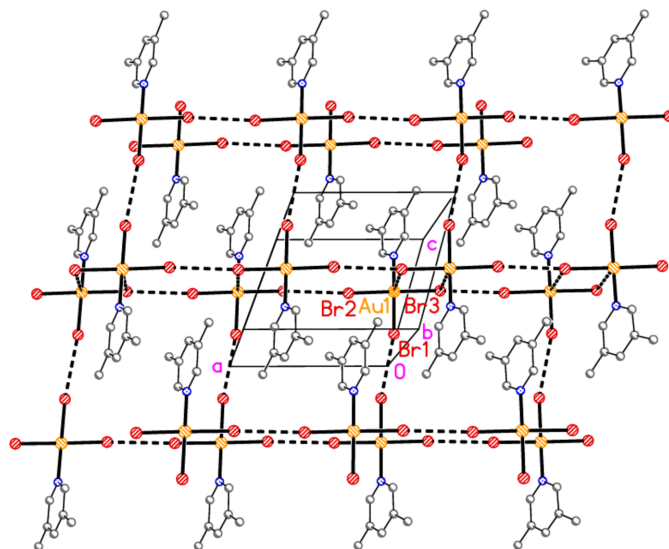
notable that the contact distances are shorter and the angles more linear for molecule **1** than for molecule **2**, for reasons that are not apparent. The main difference from **1a** is that the two chains are further linked in **4** by the contacts $\text{Br1} \cdots \text{Br6}(x, \frac{3}{2} - y, -\frac{1}{2} + z) = 3.5977(6)$ and $\text{Br3} \cdots \text{Br4} = 3.5591(6)$ Å (Fig. 21).

The packing of compound **5** resembles that of $(\text{py})\text{AuCl}$ in that the molecules are assembled into chains linked by offset stacking, with $\text{Au1} \cdots \text{Cl2}(1 - x, 1 - y, 1 - z)$ and $\text{Au1} \cdots \text{Cl2}'(x, 1 - y, \frac{1}{2} + z) = 3.6401(7)$ Å, $\text{Cl2}' \cdots \text{Au1} \cdots \text{Cl2}'' = 163.15(2)^\circ$; the chains run parallel to the *a* axis. However, the Au_2Cl_2 quadrilaterals are not edge-linked as in $(\text{py})\text{AuCl}$, but apex-linked. Similar chains were observed in the isotypic pair $(4\text{-CN-py})\text{AuX}_3$ ($X = \text{Cl}$ or Br ; Mohammad-Natij *et al.*, 2013). Adjacent chains are linked by the contact $\text{Cl2} \cdots \text{Cl2}(2 - x, y, \frac{3}{2} - z) = 3.5501(13)$ Å to form layers parallel to the *ac* plane (Fig. 22). The hydrogen bond $\text{H2} \cdots \text{Cl1}$, 2.67 Å, is not included in Fig. 22 because of the view direction, in which the rings, lying in or close to the planes at $x \simeq 0, 0.5, 1$ *etc.*, are seen edge-on. Layers are connected in the *b* direction by the three-centre hydrogen bond from H14 to two Cl2 atoms (Fig. 23).

The packing of compound **6** involves double chains, parallel to the *a* axis (Fig. 24) that are topologically the same as those of **1a** and **4**. The usual dimers are formed, although the contact distance is rather long: $\text{Au1} \cdots \text{Br3}(-x, 1 - y, 1 - z) = 3.7738(6)$ Å. The dimers are connected by the contacts


Figure 24

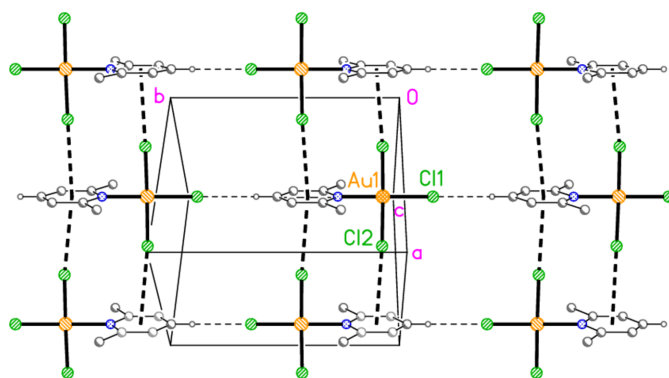
A double chain of compound **6**, viewed parallel to the *c* axis. Dashed bonds indicate $\text{Au} \cdots \text{Br}$ or $\text{Br} \cdots \text{Br}$ interactions.


Figure 25

A double layer of compound **6** parallel to the plane $(0\bar{2}1)$. The double chains of Fig. 24 are linked by $\text{Br1} \cdots \text{Br1}$ contacts [approximately vertical in this view, which is rotated by *ca* 20° around the horizontal axis from the direction perpendicular to $(0\bar{2}1)$].

$\text{Br2} \cdots \text{Br3}(1 + x, y, z) = 3.4644(6)$ Å, with angles $\text{Au1} - \text{Br2} \cdots \text{Br3}' = 165.93(2)^\circ$ and $\text{Au1} - \text{Br3} \cdots \text{Br2}' = 166.15(2)^\circ$. The double chains are connected by the contacts $\text{Br1} \cdots \text{Br1}(-x, -y, -z) = 3.4284(9)$ Å, with $\text{Au1} - \text{Br1} \cdots \text{Br1}' = 156.36(3)^\circ$, to form a double layer parallel to $(0\bar{2}1)$ (Fig. 25).

The packing of compound **7** is unexpected; it involves neither $\text{Au} \cdots \text{Cl}$ nor $\text{Cl} \cdots \text{Cl}$ interactions. Instead, the two important contacts are the short hydrogen bond $\text{H14} \cdots \text{Cl1}'(x, 1 + y, z)$ and a $\text{Cl} \cdots \pi$ contact from Cl2 to the centroid (*Cg*) of the pyridine ring at $(\frac{3}{2} - x, \frac{1}{2} - y, 1 - z)$; the contact distance $\text{Cl2} \cdots \text{Cg}'$ is 3.5458(5) Å, with angles $\text{Au1} - \text{Cl2} \cdots \text{Cg}' = 162.6^\circ$ and $\text{Cg}' \cdots \text{Cl2} \cdots \text{Cg}'' = 171.4^\circ$. The $\text{Cl} \cdots \pi$ interactions propagate parallel to $[101]$, so that the result is a layer structure parallel to $(10\bar{1})$ (Fig. 26). This type of interaction can be regarded as a halogen bond from the chlorine atom to the π electron cloud of the pyridine ligand.


Figure 26

The layer structure of compound **7** viewed perpendicular to $(10\bar{1})$. The dashed lines indicate $\text{H} \cdots \text{Cl}$ hydrogen bonds (thin) or $\text{Cl} \cdots \pi$ interactions (thick).

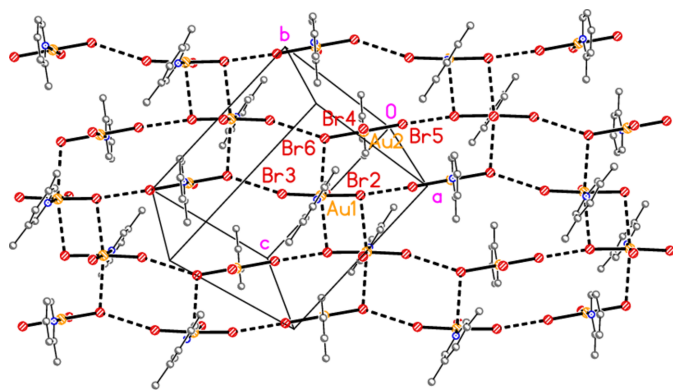


Figure 27
The layer structure of adduct **8** viewed perpendicular to (110). The dashed lines indicate Au...Br or Br...Br contacts.

The main feature of the packing of adduct **8** (composed of **2** and **6**) is a layer structure (Fig. 27) parallel to (110). Chains of alternating molecules of **2** and **6**, horizontal in Fig. 27, run parallel to $[1\bar{1}\bar{1}]$; they are propagated by the contacts $\text{Br}2 \cdots \text{Br}5(1 - x, -y, -z) = 3.2915(11) \text{ \AA}$ and $\text{Br}3 \cdots \text{Br}6(-x,$

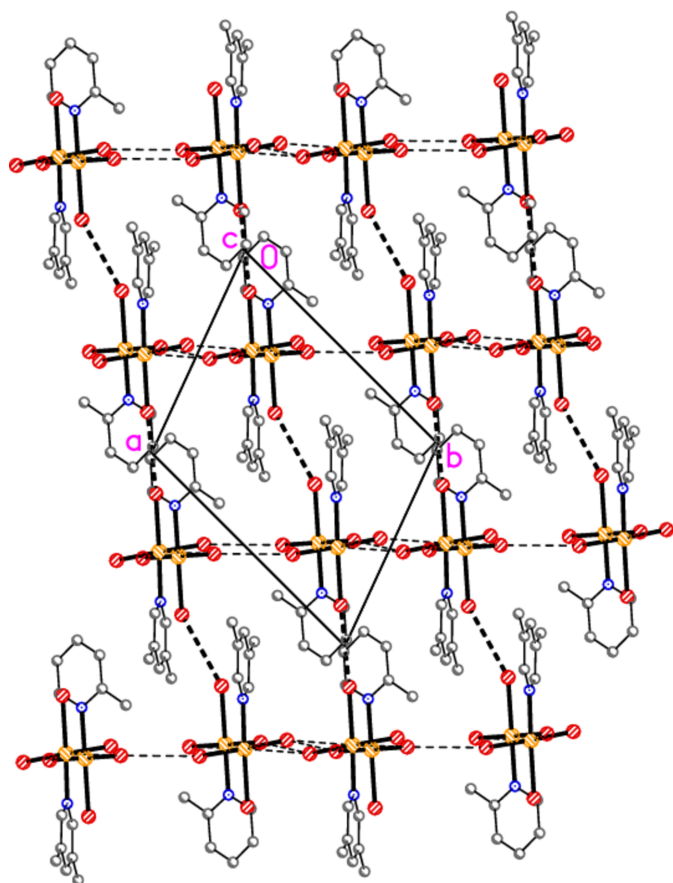


Figure 28
The links between the layers (seen edge-on) of adduct **8** are provided by the contacts $\text{Br}1 \cdots \text{Br}1'$ and $\text{Br}4 \cdots \text{Br}4'$, drawn with thick dashed lines. The former are almost exactly vertical in this diagram; the latter are slightly angled to the vertical direction. The view direction is parallel to the c axis.

$1 - y, 1 - z) = 3.5493(13) \text{ \AA}$, with $\text{Au}1 - \text{Br}2 \cdots \text{Br}5' = 161.86(5)$, $\text{Au}2 - \text{Br}5 \cdots \text{Br}2' = 169.76(5)$, $\text{Au}1 - \text{Br}3 \cdots \text{Br}6' = 162.49(5)$ and $\text{Au}2 - \text{Br}6 \cdots \text{Br}3' = 151.56(5)^\circ$. As in the structure of **2** alone, there are no axial contacts to the gold atom $\text{Au}2$ [discounting $\text{Au}2 \cdots \text{Br}2$ $3.9093(11) \text{ \AA}$ as too long]. The gold atom of molecule **6** has two axial contacts, $\text{Au}1 \cdots \text{Br}2(1 - x, -y, 1 - z) = 3.5279(10)$ and $\text{Au}1 \cdots \text{Br}6 = 3.5169(10) \text{ \AA}$, with $\text{Br}2' \cdots \text{Au}1 \cdots \text{Br}6 = 169.74(2)^\circ$, in contrast to its single axial contact in the structure of **6** alone. The former contact is part of an offset-stacked dimer (see the small quadrilaterals in Fig. 27), but these quadrilaterals do not associate directly to form more extensive elements of the packing. The linkages between layers are provided by the contacts $\text{Br}1 \cdots \text{Br}1(-x, -y, 1 - z) = 3.362(2)$ and $\text{Br}4 \cdots \text{Br}4(1 - x, 1 - y, -z) = 3.343(2) \text{ \AA}$, with $\text{Au}1 - \text{Br}1 \cdots \text{Br}1' = 175.87(7)$ and $\text{Au}2 - \text{Br}4 \cdots \text{Br}4' = 153.75(6)^\circ$ (Fig. 28), in a manner reminiscent of the interlayer links in **3** and those within the double layers of **6**.

4. Database survey

The searches employed the routine ConQuest (Bruno *et al.*, 2002), part of Version 2024.1.0 of the CSD (Groom *et al.*, 2016). A search for 'simple' compounds of the form LAuCl_3 (L = pyridine ligand with no substituents involved in further rings, X = halogen) gave 21 hits. The Au–N bond lengths were 2.015–2.073, av. 2.043 (13) \AA , the Au–Cl bond lengths *trans* to N were 2.255–2.273, av. 2.263 (3) \AA , and the Au–Cl bond lengths *cis* to Au–N were 2.221–2.29, av. 2.275 (11) \AA . No clear *trans* influences can be recognised in these values. The three hits for $X = \text{Br}$ were the $(\text{py})\text{AuBr}_3$ component of $\{[(\text{py})_2\text{AuBr}_2]^+[\text{AuBr}_4]^- \cdot [(\text{py})\text{AuBr}_3]\}$ (WOQMEU, Peters *et al.*, 2000); $(4\text{-CN-py})\text{AuBr}_3$ (WIRFUA, Mohammad-Natij *et al.*, 2013); and $(3\text{-F-py})\text{AuBr}_3$ (WEFRAE, Pizzi *et al.*, 2022). All showed $\text{Au}-\text{Br}_{\text{trans}}$ bonds significantly shorter than $\text{Au}-\text{Br}_{\text{cis}}$, by *ca* 0.02–0.03 \AA , but the Au–N bond lengths were variable at 2.040–2.098 \AA . The sample is probably too small to draw reliable conclusions.

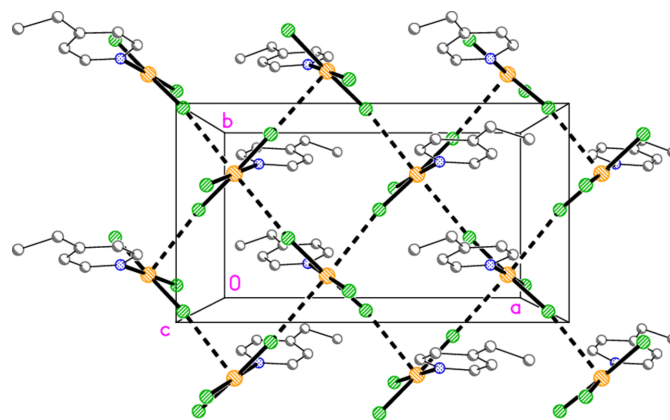
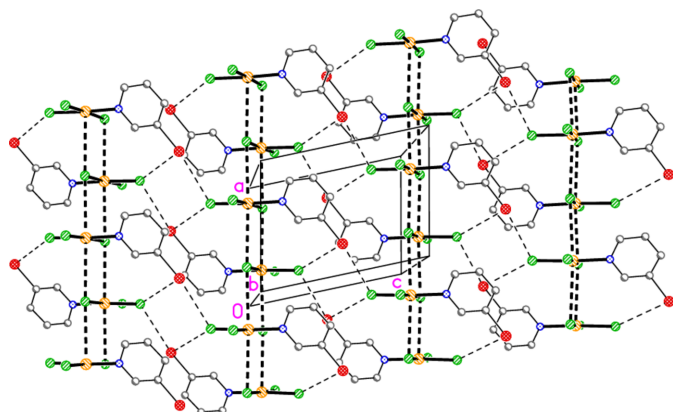
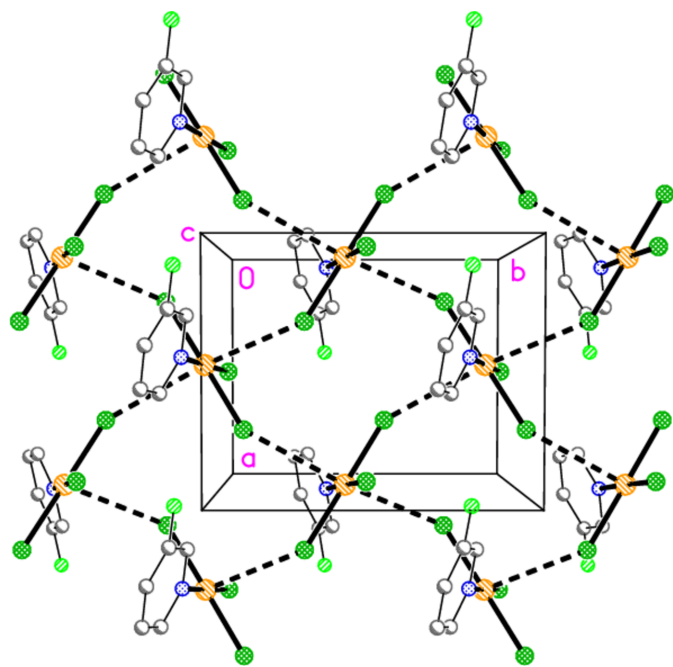


Figure 29
The packing of ESITIM, trichlorido(4-ethylpyridine)gold(III), viewed parallel to the c axis in the region $z \approx 0.75$. Dashed lines indicate Au...Cl contacts.

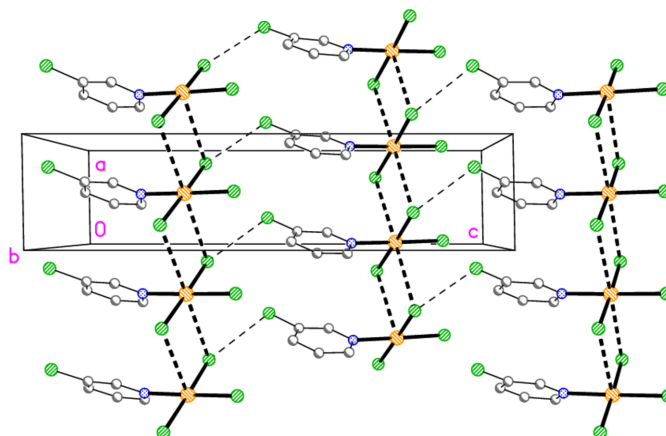

Figure 30

The packing of WEFOAD, (3-bromopyridine)trichloridogold(III), viewed perpendicular to the *ac* plane. Dashed lines indicate Au...Cl (thick) or Br...Cl (thin) contacts.

It is instructive to take six of the simplest compounds thus found and briefly compare their packing features with those of 1–8. The compounds chosen are: *L* = 4-ethylpyridine, *X* = Cl (ESITIM, Hobbollahi *et al.*, 2019); *L* = 3-bromopyridine, *X* = Cl (WEFQAD); *L* = 3-fluoropyridine, *X* = Cl (WEFQEH); *L* = 3-chloropyridine, *X* = Cl (WEFQIL); *L* = 3-iodopyridine, *X* = Cl (WEFQOR); and *L* = 3-fluoropyridine, *X* = Br (WEFRAE; all from Pizzi *et al.*, 2022). In all cases, the authors drew attention to the short Au...*X* contacts. These compounds are included in Table 19. C–H...*X* hydrogen bonding is neglected.

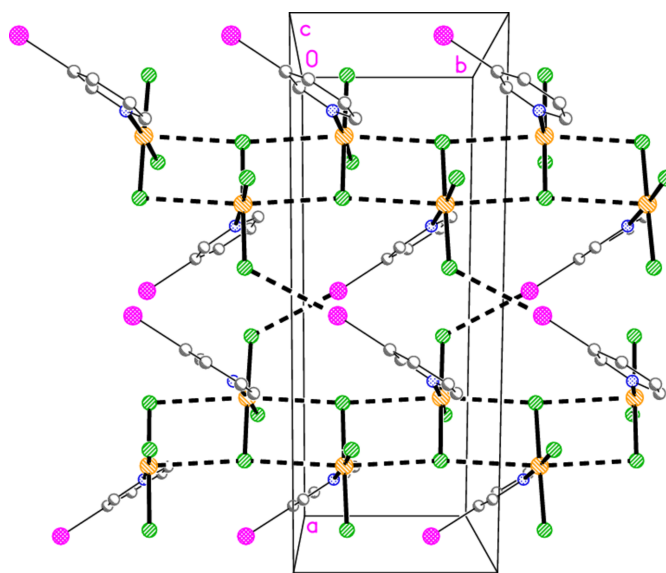

Figure 31

The packing of WEFQEH, trichlorido(3-fluoropyridine)gold(III), viewed perpendicular to the *ab* plane in the region $z \approx 0.25$. Dashed lines indicate Au...Cl contacts. Fluorine atoms are the smaller green circles. This is a redrawn version of Fig. 2 of Pizzi *et al.* (2022).


Figure 32

The packing of WEFQIL, trichlorido(3-chloropyridine)gold(III), viewed perpendicular to the *ac* plane in the region $y \approx 0.25$. Dashed lines indicate Au...Cl (thick) or Cl...Cl (thin) contacts.

ESITIM crystallizes in *Pcab* with $Z = 8$. In the original publication, the Au...Cl contacts (3.244, 3.409 Å) were described as linking the molecules to form infinite chains. In fact, they combine to form a layer structure, involving Au₄Cl₄ rings, parallel to the *ab* plane at $z \approx 0.25, 0.75$ (Fig. 29). In the series of 3-halopyridine complexes, the halogen substituents of the pyridine rings are ‘non-innocent’ atoms as regards to intermolecular interactions. In WEFOAD (*P* $\bar{1}$, $Z = 2$), the Au...Cl contacts (3.492, 3.579 Å) combine to form a ‘ladder’ structure parallel to the *a* axis. Two short Br...Cl contacts to the *trans* chlorine atom (3.490, 3.690 Å) are observed, which link the layers (Fig. 30). In the corresponding 3-fluoro derivative WEFQEH (*P*₂₁/*n*, $Z = 4$), the Au...Cl contacts (3.373, 3.426 Å) combine to form a layer structure, involving Au₄Cl₄


Figure 33

The packing of WEFQOR, trichlorido(3-iodopyridine)gold(III), viewed perpendicular to the *ab* plane in the region $z \approx 0.75$. Dashed lines indicate Au...Cl or I...Cl contacts. Iodine atoms are coloured violet.

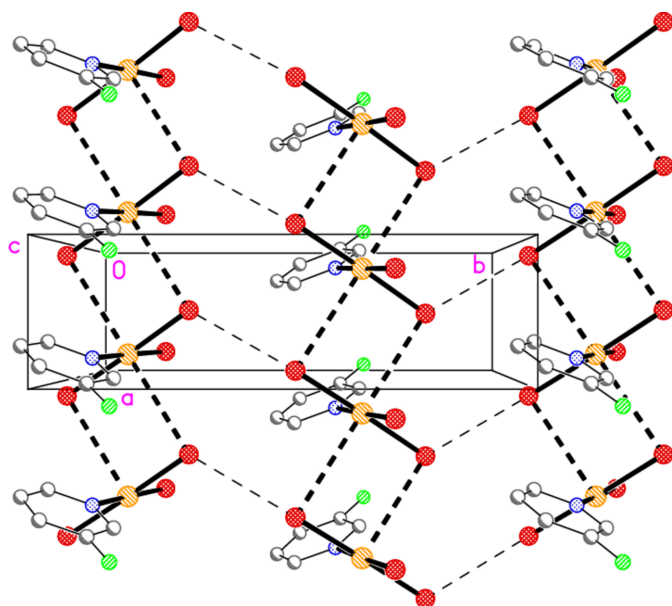


Figure 34
The packing of WEFRAE, tribromido(3-fluoropyridine)gold(III), viewed perpendicular to the *ab* plane in the region $z \simeq 0.75$. Dashed lines indicate Au...Br (thick) or Br...Br (thin) contacts. Fluorine atoms are coloured green.

rings, parallel to the *ab* plane at $z \simeq 0.25, 0.75$ (Fig. 31; an equivalent diagram was presented by Pizzi *et al.* (2022) but we include this Figure for completeness and for consistency of format). A short F...F contact of 2.684 Å links the layers. In the 3-chloro derivative WEQIL ($P2_1/n$, $Z = 4$), the Au...Cl contacts (3.402, 3.412 Å) combine to form a chain of apex-linked quadrilaterals (analogous to the chains in **5**) parallel to the *a* axis; these are linked by Cl...Cl_{py} contacts of 3.536 Å to form layers parallel to the *ac* plane at $y \simeq 0.25, 0.75$ (Fig. 32), and the layers are connected in the third dimension by another Cl...Cl_{py} contact of 3.495 Å. In the 3-iodo derivative WEQOR ($C2/c$, $Z = 8$), the Au...Cl contacts (3.368, 3.483 Å) combine to form a 'ladder' structure parallel to the *b* axis; ladders are linked by I...Cl contacts of 3.500 Å to form layers parallel to the *ab* plane at $z \simeq 0.25, 0.75$ (Fig. 33). The layers are linked in the third dimension by a Cl_{trans}...Cl_{trans} contact of 3.433 Å. In WEFRAE ($P2_12_12_1$, $Z = 4$), the tribromido analogue of WEQEH, the Au...Br contacts (3.542, 3.588 Å) combine to form a chain of apex-linked quadrilaterals parallel to the *a* axis; these are linked directly by quite long Br...Br contacts of 3.710 Å to form a layer structure parallel to the *ab* plane at $z \simeq 0.25, 0.75$ (Fig. 34). Layers are linked in the third dimension by Br_{trans}...Br_{trans} contacts of 3.712 Å. The fluorine atom is not involved in short contacts.

A search for Au^{III} structures related to **7**, containing Au—Cl and Au—N_{pyridinic} bonds together with a short Cl... π contact (defined by the distance from Cl to the pyridine ring centroid *C_g*) gave thirteen hits with Cl...*C_g* < 3.7 Å. The shortest distance is 3.344 Å in trichlorido-(1,7,15,15-tetramethyl-3,10-diazatetracyclo[10.2.1.0^{2,11}.0^{4,9}]pentadeca-2,4,-6,8,10-pentaene)gold(III), a camphorquinoxaline complex (SUYXAN; Glišić *et al.*, 2018).

5. Synthesis and crystallization

Trichlorido(2-methylpyridine)gold(III) (**1**): 114.2 mg (0.351 mmol) of the gold(I) precursor chlorido(2-methylpyridine)gold(I) was prepared by the method of Ahrens (1999). This was dissolved in 5 ml of dichloromethane, and the solution was added to a solution of 100 mg (0.363 mmol) of PhICl₂ in 5 ml of dichloromethane. Equal (0.4 ml) portions of the solution were transferred to five ignition tubes and overlaid with the five precipitants *n*-pentane, *n*-heptane, diethyl ether, diisopropyl ether and petroleum ether (b.p. 313–333 K). The tubes were stoppered and transferred to the refrigerator overnight. Crystals of compound **1**, polymorph **a**, were obtained as yellow prisms and tablets from the tube with diisopropyl ether. In general for these syntheses, crystals also formed in at least some of the other tubes, but the best, judged by inspection under a microscope, were selected for X-ray measurements. Elemental analysis [%]: calc.: C 18.18, H 1.78, N 3.53; found C 17.78, H 1.79, N 3.59. Because of the problem of incomplete oxidation that we have sometimes encountered using PhICl₂, the procedure was repeated in parallel using two equivalents of PhICl₂, although this precaution later proved to have been unnecessary for the reactions presented here. The same crystallization experiments were carried out. Crystals of compound **1**, polymorph **b**, were obtained as yellow plates from the tube with *n*-pentane. Elemental analysis [%]: calc.: C 18.18, H 1.78, N 3.53; found: C 17.63, H 1.78, N 3.58.

Tribromido(2-methylpyridine)gold(III) (**2**): 90 mg (0.247 mmol) of (tth)AuBr (tth = tetrahydrothiophene) were converted to bis(2-methylpyridine)gold(I) dibromidoaurate(I) (Döring & Jones, 2024a), which was immediately (without drying) dissolved in 2 ml of dichloromethane, and two drops of elemental bromine were added. The usual crystallization experiments were carried out. Crystals of compound **2** were obtained in the form of red blocks and tablets from the tube with *n*-pentane. Elemental analysis [%]: calc.: C 13.60, H 1.33, N 2.64; found: C 12.60, H 1.37, N 2.62.

Tribromido(3-methylpyridine)gold(III) (**3**): 90 mg (0.247 mmol) of (tth)AuBr were converted to bis(3-methylpyridine)gold(I) dibromidoaurate(I) (Döring & Jones, 2024a), which was immediately (without drying) dissolved in 2 ml of dichloromethane. Two drops of elemental bromine were added. The usual crystallization experiments were carried out. Crystals of compound **3** were obtained in the form of red plates from the tube with *n*-pentane. Elemental analysis [%]: calc.: C 13.60, H 1.33, N 2.64; found: C 13.47, H 1.35, N 2.78.

Tribromido(2,4-dimethylpyridine)gold(III) (**4**): 45.2 mg (0.124 mmol) of (tth)AuBr were dissolved in 2 ml of 2,4-dimethylpyridine. The solution was transferred to a 5 ml glass vial and overlaid with diisopropyl ether. The vial was closed and stored in the refrigerator. The supernatant was then pipetted off and the remaining colourless crystals, assumed to be bis(2,4-dimethylpyridine)gold(I) dibromidoaurate(I), dried *in vacuo*, yielded 32.5 mg (48%). The crystals proved to be unsuitable for structure determination because of streaking of the diffraction peaks. They were dissolved in 2 ml of dichloromethane and 3 drops of elemental bromine

Table 20
Experimental details.

	1a	1b	2	3	4
Crystal data					
Chemical formula	[AuCl ₃ (C ₆ H ₇ N)]	[AuCl ₃ (C ₆ H ₇ N)]	[AuBr ₃ (C ₆ H ₇ N)]	[AuBr ₃ (C ₆ H ₇ N)]	[AuBr ₃ (C ₇ H ₉ N)]
<i>M_r</i>	396.44	396.44	529.82	529.82	543.85
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Monoclinic, <i>C</i> 2/ <i>c</i>	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	100	100	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6852 (7), 14.3992 (12), 8.7963 (7)	7.8077 (8), 16.4881 (15), 7.6929 (9)	8.0776 (4), 14.7230 (7), 8.9682 (4)	18.6763 (6), 6.78409 (14), 18.4807 (5)	8.07477 (17), 17.2853 (4), 16.3527 (4)
α , β , γ (°)	90, 95.860 (8), 90	90, 103.920 (12), 90	90, 96.617 (5), 90	90, 118.887 (4), 90	90, 90.818 (2), 90
<i>V</i> (Å ³)	968.32 (14)	961.26 (18)	1059.45 (9)	2050.18 (12)	2282.19 (8)
<i>Z</i>	4	4	4	8	8
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	15.96	16.07	25.14	25.99	23.35
Crystal size (mm)	0.30 × 0.03 × 0.02	0.22 × 0.10 × 0.02	0.07 × 0.07 × 0.07	0.12 × 0.10 × 0.02	0.10 × 0.10 × 0.02
Data collection					
Diffraction	Oxford Diffraction Xcalibur, Eos	Oxford Diffraction Xcalibur, Eos	Oxford Diffraction Xcalibur, Eos	Oxford Diffraction Xcalibur, Eos	Oxford Diffraction Xcalibur, Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)
<i>T_{min}</i> , <i>T_{max}</i>	0.333, 1.000	0.254, 1.000	0.571, 1.000	0.309, 1.000	0.338, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	3572, 3572, 2943	3603, 3603, 2910	3597, 3597, 2716	40540, 3120, 2563	139727, 6677, 5614
<i>R_{int}</i>	–	–	–	0.064	0.086
θ values (°)	$\theta_{\max} = 28.3$, $\theta_{\min} = 3.4$	$\theta_{\max} = 28.3$, $\theta_{\min} = 3.0$	$\theta_{\max} = 28.3$, $\theta_{\min} = 3.2$	$\theta_{\max} = 31.0$, $\theta_{\min} = 2.5$	$\theta_{\max} = 30.0$, $\theta_{\min} = 2.4$
(sin θ/λ) _{max} (Å ⁻¹)	0.667	0.667	0.667	0.724	0.704
Refinement					
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.024, 0.049, 0.93	0.025, 0.050, 1.00	0.028, 0.040, 0.80	0.026, 0.054, 1.04	0.026, 0.048, 1.05
No. of reflections	3572	3603	3597	3120	6677
No. of parameters	102	102	102	101	222
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.86, -0.87	4.52, -0.87	1.26, -1.40	2.01, -1.71	1.39, -1.59
	5	6	7	8	
Crystal data					
Chemical formula	[AuCl ₃ (C ₇ H ₉ N)]	[AuBr ₃ (C ₇ H ₉ N)]	[AuCl ₃ (C ₇ H ₉ N)]	[AuBr ₃ (C ₇ H ₉ N)]- [AuBr ₃ (C ₆ H ₇ N)]	
<i>M_r</i>	410.47	543.85	410.47	1073.67	
Crystal system, space group	Monoclinic, <i>C</i> 2/ <i>c</i>	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>C</i> 2/ <i>c</i>	Triclinic, <i>P</i> $\bar{1}$	
Temperature (K)	100	100	100	100	
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6240 (3), 15.9360 (6), 9.2538 (4)	8.2506 (3), 8.4726 (4), 9.4210 (4)	11.0184 (3), 10.6600 (2), 9.7760 (3)	9.1741 (9), 11.1922 (9), 11.4596 (7)	
α , β , γ (°)	90, 112.333 (5), 90	113.828 (4), 103.543 (4), 98.368 (4)	90, 113.053 (3), 90	83.990 (6), 80.777 (6), 69.147 (8)	
<i>V</i> (Å ³)	1039.97 (8)	563.93 (5)	1056.55 (5)	1083.92 (16)	
<i>Z</i>	4	2	4	2	
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	
μ (mm ⁻¹)	14.86	23.62	14.63	24.58	
Crystal size (mm)	0.20 × 0.12 × 0.04	0.21 × 0.15 × 0.02	0.22 × 0.20 × 0.12	0.13 × 0.06 × 0.02	
Data collection					
Diffraction	Oxford Diffraction Xcalibur, Eos	Oxford Diffraction Xcalibur, Eos	Oxford Diffraction Xcalibur, Eos	Oxford Diffraction Xcalibur, Eos	
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)	Analytical (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)	
<i>T_{min}</i> , <i>T_{max}</i>	0.270, 1.000	0.050, 0.683	0.267, 1.000	0.052, 1.000	
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	13810, 1563, 1496	30785, 3392, 3017	15246, 1600, 1553	7479, 7479, 5015	
<i>R_{int}</i>	0.037	0.071	0.030	–	
θ values (°)	$\theta_{\max} = 30.9$, $\theta_{\min} = 2.6$	$\theta_{\max} = 31.1$, $\theta_{\min} = 2.5$	$\theta_{\max} = 31.1$, $\theta_{\min} = 2.8$	$\theta_{\max} = 28.3$, $\theta_{\min} = 2.4$	
(sin θ/λ) _{max} (Å ⁻¹)	0.722	0.727	0.726	0.667	

Table 20 (continued)

	5	6	7	8
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.014, 0.032, 1.07	0.027, 0.059, 1.06	0.013, 0.026, 1.12	0.035, 0.055, 0.82
No. of reflections	1563	3392	1600	7479
No. of parameters	58	111	59	212
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ ($e \text{ \AA}^{-3}$)	1.26, -0.88	1.61, -1.50	0.83, -1.17	2.16, -1.91

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXS97* (Sheldrick, 2008), *SHELXL2019/3* (Sheldrick, 2015) and *XP* (Bruker, 1998).

were added, leading to a red solution. This was overlaid with *n*-pentane and stored in the refrigerator for a week. Crystals of **4** were obtained in the form of red plates and needles. The elemental analysis gave an unsatisfactory value for C: [%] calc.: C 15.46, H 1.67, N 2.58; found: C 13.81, H 1.53, N 2.43.

Trichlorido(3,5-dimethylpyridine)gold(III) (**5**): 166 mg (0.518 mmol) of (tth)AuCl were converted to bis(3,5-dimethylpyridine)gold(I) dichloridoaurate(I) (Döring & Jones, 2024a). The sample was divided in half; each half was dissolved in 5 ml of dichloromethane, and then treated with one or two equivalents of PhICl₂. The solutions were subjected to the usual crystallization experiments. Crystals of **5** were obtained in the form of yellow blocks from all tubes; those chosen were from the 1:2 experiment using diethyl ether. Elemental analysis [%]: calc.: C 20.48, H 2.21, N 3.41; found: C 20.23, H 2.121, N 3.58.

Tribromido(3,5-dimethylpyridine)gold(III) (**6**): see (**8**) below.

Trichlorido(2,6-dimethylpyridine)gold(III) (**7**): 122.5 mg (0.382 mmol) of (tth)AuCl were converted to 119 mg (0.175 mmol) of (2,6-dimethylpyridine)gold(I) dichloroaurate(I) (Hashmi *et al.*, 2010). This was divided into two portions, and 2 ml of dichloromethane were added to each. A solution of 24.1 mg (0.088 mmol) of PhICl₂ in 2 ml of dichloromethane was added to one aliquot and a solution of 48.2 mg (0.175 mmol) of PhICl₂ in 2 ml of dichloromethane to the other. These solutions were subjected to the usual crystallization experiments. Crystals of **7** in the form of yellow blocks were obtained from the 1:2 experiment using *n*-heptane. Elemental analysis [%]: calc.: C 20.48, H 2.21, N 3.41; found: C 20.71, H 2.20, N 3.53.

Tribromido(2-methylpyridine)gold(III)/tribromido(3,5-dimethylpyridine)gold(III) (1/1) (**8**): Crystals of compounds **8** and **6** arose serendipitously, partly as a result of human error, as follows. 137.3 mg (0.376 mmol) of (tth)AuBr were converted to 84.0 mg (0.114 mmol) of bis(2-methylpyridine)gold(I) dibromoaurate(I) as above, of which 75.1 mg (0.102 mmol) were dissolved in 5 ml of dichloromethane. Five drops of elemental bromine were added. Half of the resulting red solution was overlaid with *n*-pentane. At some stage, which can no longer be identified (but the 2-picoline was checked by NMR and was pure), the system became contaminated with 3,5-dimethylpyridine. One of the red crystals that formed was investigated and proved to be the 1/1 adduct **8**. The ¹H NMR spectrum of the sample showed the expected two methyl singlets, but in the ratio 4:1 rather than

the expected 2:1 for a 1/1 mixture of **2** and **6**; this would suggest that the sample of red crystals from which **8** was taken consisted of both **6** and **8**. Consistent with this, the solution of the red crystals in CDCl₃, left to stand for some time, deposited a few red crystals that proved on X-ray examination to be compound **6**.

6. Refinement

Details of the measurements and refinements are given in Table 20. For all structures, multi-scan absorption corrections were applied using spherical harmonics, as implemented in the SCALE3 ABSPACK scaling algorithm (Rigaku OD, 2020). For compound **6**, analytical numeric absorption corrections using a face-indexed crystal model, based on expressions derived by Clark & Reid (1995), were applied first.

Aromatic hydrogen atoms were included at calculated positions and refined using a riding model with C—H = 0.95 Å. Methyl groups were included as idealized rigid groups with C—H = 0.98 Å and H—C—H = 109.5°, and were allowed to rotate but not tip (command 'AFIX 137'). *U* values of the hydrogen atoms were fixed at 1.5 × *U*_{eq} of the parent carbon atoms for methyl groups and 1.2 × *U*_{eq} of the parent carbon atoms for other hydrogens. A small number of badly fitting reflections were omitted (**1a**, two reflections with deviations > 8σ; **1b**, seven reflections > 7σ; **2**, one reflection > 15σ; **5**, one reflection > 6σ; **8**, one reflection > 29σ).

Four of the crystals (**1a**, **1b**, **2** and **8**) were non-merohedral twins, with twinning by 180° rotation about the *a* axis for **1a**, **1b** and **2** and about [1̄1̄1] for **8**. These structures were refined using the 'HKLf 5' method (Sheldrick, 2015). The relative volumes of the smaller twinning components refined to 0.4710 (**6**), 0.4583 (**6**), 0.4641 (**5**) and 0.4440 (**5**), respectively. The twin data reduction merges equivalent reflections before writing the intensity file, so that *R*_{int} is meaningless (and is not given in Table 20). The intensity datasets comprise all non-overlapped reflections from both components and all overlapped reflections, so that the number of reflections should be interpreted with caution. More stringent checks during the data reduction of twins (*e.g.* the command 'remove outliers') mean that the completeness of some datasets is less than ideal, typically around 95%.

Special features and exceptions: For **1b**, the large difference peak of 4.5 e Å⁻³ has coordinates that are arithmetically related to those of the gold atom and thus may represent residual twinning errors. For **3**, the *x* and *y* coordinates of the gold atom are *ca* 0.25, which leads to systematically weak

reflection classes; *checkCIF* comments on (pseudo-) *B*-centring. The second weighting parameter *b* (Sheldrick, 2015) does not converge, but oscillates over a small range. For **6**, the methyl hydrogen atoms at C18 were unclear, and were therefore refined as an ideal hexagon of half-occupied sites (command 'AFIX 127'). However, the disorder may be more extensive than this simple model.

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Crystal structures of seven gold(III) complexes of the form $LAuX_3$ (L = substituted pyridine, X = Cl or Br)

Cindy Döring and Peter G. Jones

Computing details

Trichlorido(2-methylpyridine- κ N)gold(III) (1a)

Crystal data

$[AuCl_3(C_6H_7N)]$

$M_r = 396.44$

Monoclinic, $P2_1/n$

$a = 7.6852$ (7) Å

$b = 14.3992$ (12) Å

$c = 8.7963$ (7) Å

$\beta = 95.860$ (8)°

$V = 968.32$ (14) Å³

$Z = 4$

$F(000) = 720$

$D_x = 2.719$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9050 reflections

$\theta = 3.0$ – 29.9 °

$\mu = 15.96$ mm⁻¹

$T = 100$ K

Needle, yellow

$0.30 \times 0.03 \times 0.02$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator

Detector resolution: 16.1419 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2020)

$T_{\min} = 0.333$, $T_{\max} = 1.000$

3572 measured reflections

3572 independent reflections

2943 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = -$

$\theta_{\max} = 28.3$ °, $\theta_{\min} = 3.4$ °

$h = -10 \rightarrow 10$

$k = -19 \rightarrow 19$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.049$

$S = 0.93$

3572 reflections

102 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.86$ e Å⁻³

$\Delta\rho_{\min} = -0.86$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.31798 (3)	0.60929 (2)	0.91424 (2)	0.01336 (6)
Cl1	0.3814 (2)	0.68716 (10)	1.13752 (16)	0.0235 (3)
Cl2	0.60819 (18)	0.59459 (10)	0.88550 (16)	0.0216 (3)
Cl3	0.02767 (19)	0.62595 (10)	0.93062 (17)	0.0228 (3)
N11	0.2625 (6)	0.5372 (3)	0.7158 (5)	0.0145 (10)
C12	0.2733 (7)	0.5754 (4)	0.5791 (7)	0.0180 (13)
C13	0.2423 (8)	0.5203 (4)	0.4490 (7)	0.0213 (13)
H13	0.249795	0.546607	0.350865	0.026*
C14	0.2010 (8)	0.4280 (4)	0.4621 (7)	0.0240 (14)
H14	0.181597	0.390143	0.373554	0.029*
C15	0.1879 (8)	0.3911 (4)	0.6045 (7)	0.0268 (14)
H15	0.157140	0.327702	0.615089	0.032*
C16	0.2193 (8)	0.4459 (4)	0.7300 (7)	0.0217 (14)
H16	0.211063	0.420448	0.828621	0.026*
C17	0.3146 (8)	0.6764 (4)	0.5693 (7)	0.0251 (15)
H17A	0.228129	0.712469	0.618885	0.038*
H17B	0.311091	0.694740	0.461793	0.038*
H17C	0.431574	0.688223	0.620934	0.038*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.01501 (10)	0.01177 (10)	0.01354 (10)	-0.00077 (10)	0.00270 (8)	-0.00073 (11)
Cl1	0.0311 (9)	0.0223 (8)	0.0167 (7)	-0.0007 (6)	0.0013 (6)	-0.0037 (6)
Cl2	0.0161 (7)	0.0276 (9)	0.0207 (7)	-0.0037 (6)	0.0009 (6)	-0.0014 (6)
Cl3	0.0179 (7)	0.0270 (9)	0.0239 (8)	0.0025 (6)	0.0035 (6)	-0.0025 (7)
N11	0.015 (3)	0.017 (2)	0.012 (2)	0.0020 (19)	0.0009 (19)	0.0006 (19)
C12	0.015 (3)	0.014 (3)	0.024 (3)	-0.001 (2)	0.003 (3)	0.003 (2)
C13	0.023 (4)	0.030 (4)	0.011 (3)	0.001 (3)	0.002 (2)	-0.001 (3)
C14	0.030 (4)	0.025 (3)	0.017 (3)	-0.001 (3)	0.002 (3)	-0.005 (3)
C15	0.038 (4)	0.015 (3)	0.028 (4)	-0.001 (3)	0.003 (3)	0.002 (3)
C16	0.027 (4)	0.020 (3)	0.017 (3)	-0.003 (3)	-0.001 (3)	0.001 (3)
C17	0.039 (4)	0.022 (3)	0.014 (3)	0.000 (3)	0.001 (3)	0.002 (3)

Geometric parameters (\AA , $^\circ$)

Au1—N11	2.039 (4)	C13—H13	0.9500
Au1—Cl3	2.2632 (15)	C14—C15	1.374 (8)
Au1—Cl1	2.2708 (14)	C14—H14	0.9500
Au1—Cl2	2.2799 (15)	C15—C16	1.359 (8)
N11—C12	1.333 (7)	C15—H15	0.9500
N11—C16	1.364 (7)	C16—H16	0.9500
C12—C13	1.393 (8)	C17—H17A	0.9800
C12—C17	1.493 (8)	C17—H17B	0.9800
C13—C14	1.373 (8)	C17—H17C	0.9800

N11—Au1—Cl3	89.27 (13)	C13—C14—C15	119.3 (6)
N11—Au1—Cl1	178.94 (13)	C13—C14—H14	120.3
Cl3—Au1—Cl1	91.06 (6)	C15—C14—H14	120.3
N11—Au1—Cl2	88.81 (13)	C16—C15—C14	119.5 (6)
Cl3—Au1—Cl2	177.20 (5)	C16—C15—H15	120.2
Cl1—Au1—Cl2	90.91 (5)	C14—C15—H15	120.2
C12—N11—C16	121.2 (5)	C15—C16—N11	120.7 (6)
C12—N11—Au1	122.4 (4)	C15—C16—H16	119.7
C16—N11—Au1	116.4 (4)	N11—C16—H16	119.7
N11—C12—C13	119.0 (5)	C12—C17—H17A	109.5
N11—C12—C17	119.2 (5)	C12—C17—H17B	109.5
C13—C12—C17	121.8 (5)	H17A—C17—H17B	109.5
C14—C13—C12	120.2 (6)	C12—C17—H17C	109.5
C14—C13—H13	119.9	H17A—C17—H17C	109.5
C12—C13—H13	119.9	H17B—C17—H17C	109.5
Cl3—Au1—N11—C12	101.8 (4)	N11—C12—C13—C14	0.1 (9)
Cl2—Au1—N11—C12	-76.2 (4)	C17—C12—C13—C14	-178.6 (6)
Cl3—Au1—N11—C16	-80.4 (4)	C12—C13—C14—C15	1.0 (9)
Cl2—Au1—N11—C16	101.6 (4)	C13—C14—C15—C16	-1.2 (9)
C16—N11—C12—C13	-1.0 (8)	C14—C15—C16—N11	0.4 (9)
Au1—N11—C12—C13	176.6 (4)	C12—N11—C16—C15	0.8 (9)
C16—N11—C12—C17	177.8 (5)	Au1—N11—C16—C15	-177.0 (4)
Au1—N11—C12—C17	-4.6 (7)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C13—H13···Cl1 ⁱ	0.95	3.00	3.876 (6)	153
C14—H14···Cl1 ⁱⁱ	0.95	2.96	3.617 (6)	127
C15—H15···Cl1 ⁱⁱ	0.95	3.00	3.634 (6)	126
C17—H17A···Cl1 ⁱⁱⁱ	0.98	3.05	3.964 (6)	156
C17—H17B···Cl1 ⁱ	0.98	2.96	3.888 (6)	159
C14—H14···Cl2 ^{iv}	0.95	2.93	3.538 (6)	123
C16—H16···Cl2 ^v	0.95	2.75	3.553 (6)	142
C17—H17C···Cl2	0.98	2.90	3.596 (6)	129
C14—H14···Cl3 ^{vi}	0.95	2.99	3.793 (6)	144

Symmetry codes: (i) $x, y, z-1$; (ii) $-x+1/2, y-1/2, -z+3/2$; (iii) $x-1/2, -y+3/2, z-1/2$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+1, -y+1, -z+2$; (vi) $-x, -y+1, -z+1$.Trichlorido(2-methylpyridine- κ N)gold(III) (1b)

Crystal data

[AuCl₃(C₆H₇N)] $M_r = 396.44$ Monoclinic, $P2_1/c$ $a = 7.8077$ (8) Å $b = 16.4881$ (15) Å $c = 7.6929$ (9) Å $\beta = 103.920$ (12)° $V = 961.26$ (18) Å³ $Z = 4$ $F(000) = 720$ $D_x = 2.739$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5189 reflections
 $\theta = 3.0\text{--}29.8^\circ$
 $\mu = 16.07 \text{ mm}^{-1}$

$T = 100 \text{ K}$
 Plate, yellow
 $0.22 \times 0.10 \times 0.02 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur, Eos
 diffractometer
 Radiation source: Enhance (Mo) X-ray Source
 Graphite monochromator
 Detector resolution: 16.1419 pixels mm^{-1}
 ω scan
 Absorption correction: multi-scan
 (CrysAlisPro; Rigaku OD, 2020)
 $T_{\min} = 0.254$, $T_{\max} = 1.000$

3603 measured reflections
 3603 independent reflections
 2910 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = -$
 $\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 3.0^\circ$
 $h = -10 \rightarrow 10$
 $k = -21 \rightarrow 21$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.050$
 $S = 1.00$
 3603 reflections
 102 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0258P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 4.52 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.87 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.25056 (3)	0.51656 (2)	0.21354 (3)	0.01380 (6)
Cl1	0.31201 (18)	0.38204 (8)	0.21459 (18)	0.0207 (3)
Cl2	0.2469 (2)	0.52510 (9)	-0.08269 (17)	0.0223 (3)
Cl3	0.2480 (2)	0.51253 (9)	0.50724 (19)	0.0257 (3)
N11	0.1889 (6)	0.6363 (3)	0.2071 (6)	0.0150 (9)
C12	0.3133 (7)	0.6947 (4)	0.2214 (7)	0.0175 (12)
C13	0.2617 (8)	0.7753 (4)	0.2035 (8)	0.0226 (12)
H13	0.348279	0.816701	0.214521	0.027*
C14	0.0857 (7)	0.7958 (3)	0.1698 (8)	0.0216 (12)
H14	0.050262	0.851025	0.155956	0.026*
C15	-0.0382 (8)	0.7352 (4)	0.1565 (10)	0.0230 (13)
H15	-0.160284	0.747910	0.133755	0.028*
C16	0.0171 (7)	0.6567 (4)	0.1764 (8)	0.0201 (12)
H16	-0.068217	0.614881	0.168460	0.024*
C17	0.5037 (7)	0.6680 (3)	0.2567 (10)	0.0287 (15)
H17A	0.521166	0.635987	0.155039	0.043*
H17B	0.532990	0.634864	0.365612	0.043*
H17C	0.580432	0.715824	0.272402	0.043*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.01750 (10)	0.01050 (9)	0.01386 (9)	-0.00089 (10)	0.00467 (7)	-0.00015 (10)
C11	0.0253 (7)	0.0121 (7)	0.0248 (7)	0.0018 (5)	0.0061 (6)	0.0012 (5)
C12	0.0381 (8)	0.0163 (7)	0.0138 (7)	-0.0021 (6)	0.0088 (7)	-0.0005 (5)
C13	0.0375 (8)	0.0243 (8)	0.0174 (7)	0.0053 (7)	0.0105 (7)	0.0011 (6)
N11	0.019 (2)	0.008 (2)	0.017 (2)	0.0010 (17)	0.0030 (19)	-0.0011 (19)
C12	0.018 (3)	0.018 (3)	0.017 (3)	-0.002 (2)	0.005 (2)	-0.001 (2)
C13	0.025 (3)	0.015 (3)	0.027 (3)	-0.003 (3)	0.006 (3)	-0.001 (3)
C14	0.027 (3)	0.013 (3)	0.026 (3)	0.003 (2)	0.008 (3)	0.000 (2)
C15	0.021 (3)	0.022 (3)	0.026 (3)	0.004 (2)	0.005 (3)	-0.007 (3)
C16	0.018 (3)	0.017 (3)	0.026 (3)	-0.005 (2)	0.007 (2)	-0.006 (3)
C17	0.021 (3)	0.016 (3)	0.049 (4)	-0.004 (2)	0.007 (3)	0.001 (3)

Geometric parameters (\AA , $^\circ$)

Au1—N11	2.030 (4)	C13—H13	0.9500
Au1—C13	2.2652 (14)	C14—C15	1.378 (8)
Au1—C11	2.2688 (13)	C14—H14	0.9500
Au1—C12	2.2766 (12)	C15—C16	1.361 (8)
N11—C16	1.347 (6)	C15—H15	0.9500
N11—C12	1.354 (7)	C16—H16	0.9500
C12—C13	1.385 (8)	C17—H17A	0.9800
C12—C17	1.512 (7)	C17—H17B	0.9800
C13—C14	1.378 (7)	C17—H17C	0.9800
N11—Au1—C13	89.65 (14)	C13—C14—C15	119.1 (6)
N11—Au1—C11	178.32 (13)	C13—C14—H14	120.4
C13—Au1—C11	91.17 (5)	C15—C14—H14	120.4
N11—Au1—C12	88.27 (13)	C16—C15—C14	118.9 (6)
C13—Au1—C12	177.79 (5)	C16—C15—H15	120.6
C11—Au1—C12	90.90 (5)	C14—C15—H15	120.6
C16—N11—C12	120.1 (5)	N11—C16—C15	122.2 (5)
C16—N11—Au1	117.9 (4)	N11—C16—H16	118.9
C12—N11—Au1	121.9 (4)	C15—C16—H16	118.9
N11—C12—C13	119.3 (5)	C12—C17—H17A	109.5
N11—C12—C17	117.5 (5)	C12—C17—H17B	109.5
C13—C12—C17	123.2 (5)	H17A—C17—H17B	109.5
C14—C13—C12	120.5 (5)	C12—C17—H17C	109.5
C14—C13—H13	119.8	H17A—C17—H17C	109.5
C12—C13—H13	119.8	H17B—C17—H17C	109.5
C13—Au1—N11—C16	-86.0 (4)	N11—C12—C13—C14	-0.6 (8)
C12—Au1—N11—C16	93.3 (4)	C17—C12—C13—C14	179.4 (6)
C13—Au1—N11—C12	98.2 (4)	C12—C13—C14—C15	0.8 (9)
C12—Au1—N11—C12	-82.5 (4)	C13—C14—C15—C16	-0.2 (10)
C16—N11—C12—C13	-0.2 (8)	C12—N11—C16—C15	0.9 (9)

Au1—N11—C12—C13	175.5 (4)	Au1—N11—C16—C15	−175.0 (5)
C16—N11—C12—C17	179.7 (5)	C14—C15—C16—N11	−0.6 (10)
Au1—N11—C12—C17	−4.6 (7)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C13—H13...C11 ⁱ	0.95	2.79	3.683 (6)	157
C15—H15...C11 ⁱⁱ	0.95	2.88	3.527 (6)	126
C17—H17C...C11 ⁱ	0.98	2.86	3.798 (6)	160
C16—H16...C12 ⁱⁱⁱ	0.95	2.70	3.610 (6)	162
C17—H17B...C13 ^{iv}	0.98	3.00	3.771 (6)	137

Symmetry codes: (i) $-x+1, y+1/2, -z+1/2$; (ii) $-x, y+1/2, -z+1/2$; (iii) $-x, -y+1, -z$; (iv) $-x+1, -y+1, -z+1$.

Tribromido(2-methylpyridine- κ N)gold(III) (2)

Crystal data

[AuBr₃(C₆H₇N)]

$M_r = 529.82$

Monoclinic, $P2_1/n$

$a = 8.0776$ (4) Å

$b = 14.7230$ (7) Å

$c = 8.9682$ (4) Å

$\beta = 96.617$ (5)°

$V = 1059.45$ (9) Å³

$Z = 4$

$F(000) = 936$

$D_x = 3.322$ Mg m^{−3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7970 reflections

$\theta = 3.2$ – 29.2 °

$\mu = 25.14$ mm^{−1}

$T = 100$ K

Cube, red

$0.07 \times 0.07 \times 0.07$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator

Detector resolution: 16.1419 pixels mm^{−1}

ω scans

Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2020)

$T_{\min} = 0.571$, $T_{\max} = 1.000$

3597 measured reflections

3597 independent reflections

2716 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = -$

$\theta_{\max} = 28.3$ °, $\theta_{\min} = 3.2$ °

$h = -10$ → 10

$k = -19$ → 19

$l = -11$ → 11

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.040$

$S = 0.80$

3597 reflections

102 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0102P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.26$ e Å^{−3}

$\Delta\rho_{\min} = -1.40$ e Å^{−3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.32350 (4)	0.61053 (2)	0.91242 (3)	0.01172 (7)
Br1	0.39636 (9)	0.69112 (5)	1.14322 (8)	0.01898 (18)
Br2	0.61485 (9)	0.59456 (5)	0.87711 (8)	0.01859 (19)
Br3	0.03134 (9)	0.62958 (5)	0.93519 (8)	0.01940 (19)
N11	0.2616 (7)	0.5394 (3)	0.7174 (6)	0.0123 (14)
C12	0.2659 (8)	0.5774 (5)	0.5798 (7)	0.0125 (16)
C13	0.2314 (9)	0.5240 (5)	0.4544 (8)	0.0198 (19)
H13	0.235011	0.549813	0.357770	0.024*
C14	0.1919 (9)	0.4339 (5)	0.4666 (8)	0.0202 (19)
H14	0.169881	0.397384	0.379219	0.024*
C15	0.1846 (9)	0.3971 (5)	0.6052 (8)	0.0194 (16)
H15	0.155268	0.335136	0.615523	0.023*
C16	0.2203 (9)	0.4512 (5)	0.7299 (8)	0.0197 (18)
H16	0.215791	0.425899	0.826817	0.024*
C17	0.3074 (8)	0.6761 (4)	0.5701 (7)	0.0181 (18)
H17A	0.226556	0.712064	0.618463	0.027*
H17B	0.303266	0.693940	0.464416	0.027*
H17C	0.419646	0.687021	0.620966	0.027*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.01248 (15)	0.01227 (12)	0.01070 (13)	−0.00019 (14)	0.00261 (11)	−0.00070 (14)
Br1	0.0246 (5)	0.0187 (4)	0.0136 (4)	−0.0007 (4)	0.0021 (3)	−0.0033 (3)
Br2	0.0137 (4)	0.0249 (5)	0.0175 (4)	−0.0014 (4)	0.0034 (3)	−0.0014 (4)
Br3	0.0139 (4)	0.0250 (4)	0.0197 (4)	0.0033 (3)	0.0039 (3)	−0.0007 (4)
N11	0.016 (4)	0.012 (3)	0.010 (3)	0.000 (3)	0.004 (3)	0.000 (3)
C12	0.009 (4)	0.015 (4)	0.014 (4)	0.006 (3)	0.005 (3)	0.001 (3)
C13	0.022 (5)	0.027 (5)	0.010 (4)	0.000 (4)	0.003 (4)	0.008 (3)
C14	0.025 (5)	0.019 (4)	0.015 (4)	−0.002 (4)	−0.003 (4)	−0.007 (3)
C15	0.022 (4)	0.013 (4)	0.023 (4)	−0.004 (4)	0.000 (3)	−0.003 (4)
C16	0.017 (5)	0.017 (4)	0.025 (4)	−0.001 (4)	0.003 (4)	0.005 (4)
C17	0.027 (5)	0.018 (4)	0.010 (4)	−0.004 (4)	0.005 (3)	0.006 (3)

Geometric parameters (\AA , $^\circ$)

Au1—N11	2.050 (5)	C13—H13	0.9500
Au1—Br1	2.3996 (7)	C14—C15	1.363 (9)
Au1—Br3	2.4085 (8)	C14—H14	0.9500
Au1—Br2	2.4220 (8)	C15—C16	1.377 (8)
N11—C16	1.349 (7)	C15—H15	0.9500
N11—C12	1.359 (8)	C16—H16	0.9500
C12—C13	1.375 (8)	C17—H17A	0.9800
C12—C17	1.496 (9)	C17—H17B	0.9800
C13—C14	1.372 (9)	C17—H17C	0.9800

N11—Au1—Br1	178.93 (15)	C15—C14—C13	119.5 (7)
N11—Au1—Br3	89.24 (16)	C15—C14—H14	120.3
Br1—Au1—Br3	90.84 (3)	C13—C14—H14	120.3
N11—Au1—Br2	89.08 (16)	C14—C15—C16	119.0 (7)
Br1—Au1—Br2	90.88 (3)	C14—C15—H15	120.5
Br3—Au1—Br2	177.16 (3)	C16—C15—H15	120.5
C16—N11—C12	120.3 (6)	N11—C16—C15	121.4 (7)
C16—N11—Au1	117.3 (5)	N11—C16—H16	119.3
C12—N11—Au1	122.4 (4)	C15—C16—H16	119.3
N11—C12—C13	118.9 (6)	C12—C17—H17A	109.5
N11—C12—C17	118.8 (6)	C12—C17—H17B	109.5
C13—C12—C17	122.3 (6)	H17A—C17—H17B	109.5
C14—C13—C12	121.0 (7)	C12—C17—H17C	109.5
C14—C13—H13	119.5	H17A—C17—H17C	109.5
C12—C13—H13	119.5	H17B—C17—H17C	109.5
Br3—Au1—N11—C16	−80.7 (5)	N11—C12—C13—C14	0.5 (10)
Br2—Au1—N11—C16	101.6 (5)	C17—C12—C13—C14	−179.3 (7)
Br3—Au1—N11—C12	101.2 (5)	C12—C13—C14—C15	0.9 (11)
Br2—Au1—N11—C12	−76.5 (5)	C13—C14—C15—C16	−1.2 (11)
C16—N11—C12—C13	−1.5 (10)	C12—N11—C16—C15	1.2 (10)
Au1—N11—C12—C13	176.5 (5)	Au1—N11—C16—C15	−176.9 (5)
C16—N11—C12—C17	178.2 (6)	C14—C15—C16—N11	0.2 (11)
Au1—N11—C12—C17	−3.7 (8)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C13—H13···Br1 ⁱ	0.95	3.21	4.059 (7)	150
C14—H14···Br1 ⁱⁱ	0.95	3.09	3.754 (7)	129
C15—H15···Br1 ⁱⁱⁱ	0.95	3.14	3.775 (7)	126
C17—H17A···Br1 ⁱⁱⁱ	0.98	3.05	3.972 (7)	156
C17—H17B···Br1 ⁱ	0.98	3.06	3.982 (6)	157
C14—H14···Br2 ^{iv}	0.95	3.04	3.636 (7)	122
C16—H16···Br2 ^v	0.95	2.86	3.683 (7)	146
C17—H17C···Br2	0.98	2.96	3.690 (7)	132
C14—H14···Br3 ^{vi}	0.95	3.11	3.951 (7)	148

Symmetry codes: (i) $x, y, z-1$; (ii) $-x+1/2, y-1/2, -z+3/2$; (iii) $x-1/2, -y+3/2, z-1/2$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+1, -y+1, -z+2$; (vi) $-x, -y+1, -z+1$.

Tribromido(3-methylpyridine- κ N)gold(III) (3)

Crystal data

[AuBr₃(C₆H₇N)]
 $M_r = 529.82$
 Monoclinic, $C2/c$
 $a = 18.6763$ (6) Å
 $b = 6.78409$ (14) Å
 $c = 18.4807$ (5) Å

$\beta = 118.887$ (4)°
 $V = 2050.18$ (12) Å³
 $Z = 8$
 $F(000) = 1872$
 $D_x = 3.433$ Mg m^{−3}
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7609 reflections
 $\theta = 2.5\text{--}30.2^\circ$
 $\mu = 25.99 \text{ mm}^{-1}$

$T = 100 \text{ K}$
 Plate, red
 $0.12 \times 0.10 \times 0.02 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur, Eos
 diffractometer
 Radiation source: Enhance (Mo) X-ray Source
 Detector resolution: 16.1419 pixels mm^{-1}
 ω scan
 Absorption correction: multi-scan
 (CrysAlisPro; Rigaku OD, 2020)
 $T_{\min} = 0.309$, $T_{\max} = 1.000$

40540 measured reflections
 3120 independent reflections
 2563 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$
 $\theta_{\max} = 31.0^\circ$, $\theta_{\min} = 2.5^\circ$
 $h = -26 \rightarrow 26$
 $k = -9 \rightarrow 9$
 $l = -25 \rightarrow 26$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.054$
 $S = 1.04$
 3120 reflections
 101 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0194P)^2 + 10.7877P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.01 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.71 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.25213 (2)	0.25929 (2)	0.37416 (2)	0.01140 (5)
Br1	0.10545 (3)	0.26127 (7)	0.29684 (3)	0.01921 (10)
Br2	0.25822 (3)	0.55197 (7)	0.30223 (3)	0.01973 (11)
Br3	0.24913 (3)	-0.02193 (7)	0.45387 (3)	0.01697 (10)
N11	0.3782 (2)	0.2527 (5)	0.4343 (2)	0.0120 (7)
C12	0.4162 (3)	0.2409 (6)	0.3884 (3)	0.0135 (8)
H12	0.384098	0.233363	0.329940	0.016*
C13	0.4998 (3)	0.2393 (6)	0.4233 (3)	0.0142 (9)
C14	0.5454 (3)	0.2506 (6)	0.5089 (3)	0.0151 (9)
H14	0.603448	0.250258	0.534980	0.018*
C15	0.5065 (3)	0.2623 (6)	0.5564 (3)	0.0150 (9)
H15	0.537267	0.269624	0.614938	0.018*
C16	0.4220 (3)	0.2631 (6)	0.5169 (3)	0.0141 (9)
H16	0.394516	0.271021	0.548698	0.017*
C17	0.5387 (3)	0.2290 (7)	0.3688 (3)	0.0205 (10)
H17A	0.503831	0.151818	0.319215	0.031*
H17B	0.592426	0.165859	0.398891	0.031*
H17C	0.545228	0.362545	0.352579	0.031*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.00696 (8)	0.01682 (9)	0.00889 (8)	0.00109 (6)	0.00261 (6)	0.00037 (6)
Br1	0.0074 (2)	0.0358 (3)	0.0120 (2)	0.00234 (19)	0.00275 (17)	0.00061 (18)
Br2	0.0159 (2)	0.0234 (2)	0.0155 (2)	0.00211 (18)	0.00399 (18)	0.00782 (18)
Br3	0.0128 (2)	0.0176 (2)	0.0204 (2)	0.00011 (17)	0.00787 (18)	0.00323 (17)
N11	0.0085 (18)	0.0128 (16)	0.0128 (17)	0.0012 (14)	0.0035 (14)	0.0017 (14)
C12	0.013 (2)	0.015 (2)	0.0097 (19)	-0.0018 (17)	0.0032 (17)	-0.0018 (16)
C13	0.012 (2)	0.013 (2)	0.014 (2)	-0.0020 (17)	0.0037 (17)	-0.0006 (16)
C14	0.010 (2)	0.013 (2)	0.015 (2)	-0.0001 (17)	0.0000 (17)	-0.0013 (17)
C15	0.011 (2)	0.016 (2)	0.013 (2)	-0.0004 (17)	0.0026 (17)	-0.0010 (17)
C16	0.016 (2)	0.012 (2)	0.013 (2)	-0.0002 (17)	0.0065 (18)	0.0013 (16)
C17	0.015 (2)	0.030 (3)	0.019 (2)	-0.001 (2)	0.010 (2)	-0.0009 (19)

Geometric parameters (\AA , $^\circ$)

Au1—N11	2.062 (4)	C13—C17	1.501 (6)
Au1—Br1	2.4009 (5)	C14—C15	1.386 (6)
Au1—Br2	2.4225 (5)	C14—H14	0.9500
Au1—Br3	2.4276 (5)	C15—C16	1.382 (6)
N11—C16	1.341 (6)	C15—H15	0.9500
N11—C12	1.346 (6)	C16—H16	0.9500
C12—C13	1.372 (6)	C17—H17A	0.9800
C12—H12	0.9500	C17—H17B	0.9800
C13—C14	1.391 (6)	C17—H17C	0.9800
N11—Au1—Br1	176.62 (10)	C15—C14—C13	120.3 (4)
N11—Au1—Br2	88.25 (10)	C15—C14—H14	119.9
Br1—Au1—Br2	90.649 (17)	C13—C14—H14	119.9
N11—Au1—Br3	90.63 (10)	C16—C15—C14	118.7 (4)
Br1—Au1—Br3	90.653 (17)	C16—C15—H15	120.7
Br2—Au1—Br3	176.494 (17)	C14—C15—H15	120.7
C16—N11—C12	120.3 (4)	N11—C16—C15	120.9 (4)
C16—N11—Au1	121.4 (3)	N11—C16—H16	119.5
C12—N11—Au1	118.3 (3)	C15—C16—H16	119.5
N11—C12—C13	122.1 (4)	C13—C17—H17A	109.5
N11—C12—H12	119.0	C13—C17—H17B	109.5
C13—C12—H12	119.0	H17A—C17—H17B	109.5
C12—C13—C14	117.8 (4)	C13—C17—H17C	109.5
C12—C13—C17	119.6 (4)	H17A—C17—H17C	109.5
C14—C13—C17	122.5 (4)	H17B—C17—H17C	109.5
Br2—Au1—N11—C16	120.5 (3)	N11—C12—C13—C17	-179.1 (4)
Br3—Au1—N11—C16	-56.1 (3)	C12—C13—C14—C15	0.2 (6)
Br2—Au1—N11—C12	-58.4 (3)	C17—C13—C14—C15	179.2 (4)
Br3—Au1—N11—C12	124.9 (3)	C13—C14—C15—C16	-0.2 (6)
C16—N11—C12—C13	-0.1 (6)	C12—N11—C16—C15	0.2 (6)

Au1—N11—C12—C13	178.8 (3)	Au1—N11—C16—C15	-178.8 (3)
N11—C12—C13—C14	0.0 (6)	C14—C15—C16—N11	0.0 (6)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C15—H15···Br1 ⁱ	0.95	2.97	3.905 (5)	168
C16—H16···Br1 ⁱⁱ	0.95	2.86	3.721 (5)	151
C12—H12···Br2 ⁱⁱⁱ	0.95	2.88	3.684 (4)	144
C14—H14···Br3 ^{iv}	0.95	3.08	3.880 (5)	143
C17—H17B···Br3 ^{iv}	0.98	3.06	3.984 (5)	159

Symmetry codes: (i) $x+1/2, -y+1/2, z+1/2$; (ii) $-x+1/2, -y+1/2, -z+1$; (iii) $-x+1/2, y-1/2, -z+1/2$; (iv) $-x+1, -y, -z+1$.

Tribromido(2,4-dimethylpyridine- κ N)gold(III) (4)*Crystal data*[AuBr₃(C₇H₉N)] $M_r = 543.85$ Monoclinic, $P2_1/c$ $a = 8.07477$ (17) Å $b = 17.2853$ (4) Å $c = 16.3527$ (4) Å $\beta = 90.818$ (2)° $V = 2282.19$ (8) Å³ $Z = 8$ $F(000) = 1936$ $D_x = 3.166$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 19274 reflections

 $\theta = 2.5$ – 30.3 ° $\mu = 23.35$ mm⁻¹ $T = 100$ K

Plate, red

 $0.10 \times 0.10 \times 0.02$ mm*Data collection*Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1419 pixels mm⁻¹ ω scan

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2020)

 $T_{\min} = 0.338, T_{\max} = 1.000$

139727 measured reflections

6677 independent reflections

5614 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.086$ $\theta_{\text{max}} = 30.0$ °, $\theta_{\text{min}} = 2.4$ ° $h = -11 \rightarrow 11$ $k = -24 \rightarrow 24$ $l = -22 \rightarrow 22$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.026$ $wR(F^2) = 0.048$ $S = 1.05$

6677 reflections

222 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0166P)^2 + 4.8838P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 1.39$ e Å⁻³ $\Delta\rho_{\text{min}} = -1.59$ e Å⁻³Extinction correction: SHELXL-2019/3
(Sheldrick, 2015), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.000318 (17)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.37066 (2)	0.53353 (2)	0.11463 (2)	0.01033 (4)
Br1	0.35705 (5)	0.66385 (2)	0.06436 (3)	0.01563 (9)
Br2	0.66835 (5)	0.53128 (2)	0.09789 (3)	0.01426 (9)
Br3	0.07450 (5)	0.53012 (3)	0.12900 (3)	0.01837 (10)
N11	0.3818 (4)	0.4216 (2)	0.1579 (2)	0.0121 (7)
C12	0.4170 (5)	0.4049 (3)	0.2370 (3)	0.0130 (8)
C13	0.4288 (5)	0.3282 (3)	0.2610 (3)	0.0151 (9)
H13	0.454690	0.316512	0.316517	0.018*
C14	0.4035 (5)	0.2683 (3)	0.2061 (3)	0.0162 (9)
C15	0.3669 (5)	0.2879 (3)	0.1251 (3)	0.0150 (9)
H15	0.348718	0.248629	0.085306	0.018*
C16	0.3573 (5)	0.3649 (3)	0.1036 (3)	0.0166 (9)
H16	0.332571	0.378020	0.048345	0.020*
C17	0.4415 (6)	0.4704 (3)	0.2961 (3)	0.0183 (9)
H17A	0.530902	0.503920	0.277120	0.027*
H17B	0.470737	0.449597	0.350165	0.027*
H17C	0.338832	0.500328	0.299634	0.027*
C18	0.4170 (6)	0.1852 (3)	0.2307 (3)	0.0244 (11)
H18A	0.531110	0.167388	0.223336	0.037*
H18B	0.341891	0.153968	0.196547	0.037*
H18C	0.386945	0.179641	0.288221	0.037*
Au2	0.05459 (2)	0.61831 (2)	0.47994 (2)	0.01028 (4)
Br4	0.04989 (6)	0.59206 (3)	0.33604 (3)	0.01625 (9)
Br5	-0.23631 (5)	0.58457 (3)	0.48885 (3)	0.01582 (9)
Br6	0.34824 (5)	0.64545 (3)	0.47627 (3)	0.01783 (9)
N21	0.0611 (4)	0.6427 (2)	0.6029 (2)	0.0109 (7)
C22	-0.0021 (5)	0.7083 (2)	0.6339 (3)	0.0125 (8)
C23	0.0127 (5)	0.7219 (3)	0.7175 (3)	0.0141 (9)
H23	-0.029797	0.768577	0.739524	0.017*
C24	0.0882 (6)	0.6686 (3)	0.7695 (3)	0.0157 (9)
C25	0.1492 (5)	0.6013 (2)	0.7343 (3)	0.0138 (9)
H25	0.200804	0.563014	0.767731	0.017*
C26	0.1350 (5)	0.5900 (2)	0.6520 (3)	0.0139 (9)
H26	0.178270	0.544038	0.628684	0.017*
C27	-0.0856 (6)	0.7651 (3)	0.5782 (3)	0.0166 (9)
H27A	-0.015775	0.774566	0.530717	0.025*
H27B	-0.103312	0.813776	0.607504	0.025*
H27C	-0.192617	0.744148	0.559799	0.025*
C28	0.1065 (6)	0.6835 (3)	0.8595 (3)	0.0225 (11)
H28A	0.214812	0.707064	0.870927	0.034*
H28B	0.098020	0.634500	0.889310	0.034*
H28C	0.018761	0.718645	0.877136	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.00968 (8)	0.00956 (8)	0.01173 (8)	0.00064 (6)	-0.00049 (6)	0.00167 (6)
Br1	0.0168 (2)	0.0106 (2)	0.0194 (2)	0.00176 (16)	-0.00143 (17)	0.00387 (16)
Br2	0.00955 (19)	0.0156 (2)	0.0176 (2)	0.00043 (16)	-0.00044 (16)	0.00493 (16)
Br3	0.0101 (2)	0.0200 (2)	0.0250 (2)	0.00089 (17)	0.00161 (17)	0.00309 (18)
N11	0.0124 (17)	0.0114 (18)	0.0124 (17)	0.0013 (14)	0.0008 (14)	0.0008 (14)
C12	0.0079 (19)	0.017 (2)	0.014 (2)	-0.0007 (16)	0.0059 (16)	0.0008 (17)
C13	0.017 (2)	0.016 (2)	0.013 (2)	-0.0017 (17)	-0.0005 (17)	0.0037 (17)
C14	0.012 (2)	0.015 (2)	0.021 (2)	0.0010 (17)	0.0005 (17)	0.0049 (18)
C15	0.015 (2)	0.014 (2)	0.016 (2)	0.0001 (17)	-0.0012 (17)	-0.0027 (17)
C16	0.016 (2)	0.017 (2)	0.017 (2)	-0.0007 (17)	-0.0017 (18)	0.0011 (17)
C17	0.021 (2)	0.016 (2)	0.018 (2)	-0.0007 (19)	-0.0022 (18)	-0.0007 (18)
C18	0.032 (3)	0.015 (2)	0.026 (3)	0.001 (2)	-0.005 (2)	0.005 (2)
Au2	0.01084 (8)	0.00909 (8)	0.01092 (8)	0.00035 (6)	0.00056 (6)	-0.00007 (6)
Br4	0.0218 (2)	0.0154 (2)	0.0117 (2)	0.00044 (17)	0.00153 (17)	-0.00077 (16)
Br5	0.0116 (2)	0.0174 (2)	0.0184 (2)	-0.00171 (16)	0.00051 (16)	-0.00224 (17)
Br6	0.0121 (2)	0.0191 (2)	0.0223 (2)	-0.00219 (17)	0.00266 (17)	-0.00037 (18)
N21	0.0082 (16)	0.0091 (17)	0.0155 (18)	-0.0009 (13)	-0.0010 (14)	0.0004 (14)
C22	0.010 (2)	0.011 (2)	0.017 (2)	-0.0029 (16)	-0.0015 (16)	0.0004 (16)
C23	0.014 (2)	0.016 (2)	0.013 (2)	-0.0004 (17)	0.0030 (16)	-0.0002 (17)
C24	0.018 (2)	0.017 (2)	0.012 (2)	-0.0076 (18)	-0.0016 (17)	-0.0004 (17)
C25	0.014 (2)	0.013 (2)	0.014 (2)	-0.0005 (16)	-0.0019 (17)	0.0028 (16)
C26	0.014 (2)	0.011 (2)	0.017 (2)	0.0015 (16)	-0.0021 (17)	0.0010 (16)
C27	0.021 (2)	0.010 (2)	0.018 (2)	0.0028 (17)	-0.0009 (18)	-0.0024 (17)
C28	0.033 (3)	0.022 (3)	0.013 (2)	-0.002 (2)	-0.005 (2)	-0.0034 (18)

Geometric parameters (Å, °)

Au1—N11	2.062 (3)	Au2—N21	2.054 (4)
Au1—Br1	2.3998 (4)	Au2—Br4	2.3963 (4)
Au1—Br3	2.4070 (5)	Au2—Br6	2.4187 (5)
Au1—Br2	2.4235 (4)	Au2—Br5	2.4266 (5)
N11—C16	1.336 (5)	N21—C22	1.346 (5)
N11—C12	1.350 (5)	N21—C26	1.348 (5)
C12—C13	1.385 (6)	C22—C23	1.390 (6)
C12—C17	1.500 (6)	C22—C27	1.493 (6)
C13—C14	1.384 (6)	C23—C24	1.388 (6)
C13—H13	0.9500	C23—H23	0.9500
C14—C15	1.394 (6)	C24—C25	1.392 (6)
C14—C18	1.496 (6)	C24—C28	1.499 (6)
C15—C16	1.379 (6)	C25—C26	1.364 (6)
C15—H15	0.9500	C25—H25	0.9500
C16—H16	0.9500	C26—H26	0.9500
C17—H17A	0.9800	C27—H27A	0.9800
C17—H17B	0.9800	C27—H27B	0.9800
C17—H17C	0.9800	C27—H27C	0.9800

C18—H18A	0.9800	C28—H28A	0.9800
C18—H18B	0.9800	C28—H28B	0.9800
C18—H18C	0.9800	C28—H28C	0.9800
N11—Au1—Br1	179.86 (11)	N21—Au2—Br4	178.91 (10)
N11—Au1—Br3	88.97 (10)	N21—Au2—Br6	88.46 (10)
Br1—Au1—Br3	90.901 (16)	Br4—Au2—Br6	90.810 (16)
N11—Au1—Br2	89.16 (10)	N21—Au2—Br5	90.10 (10)
Br1—Au1—Br2	90.974 (15)	Br4—Au2—Br5	90.672 (16)
Br3—Au1—Br2	177.518 (17)	Br6—Au2—Br5	176.590 (17)
C16—N11—C12	120.5 (4)	C22—N21—C26	120.8 (4)
C16—N11—Au1	117.0 (3)	C22—N21—Au2	122.5 (3)
C12—N11—Au1	122.5 (3)	C26—N21—Au2	116.7 (3)
N11—C12—C13	119.3 (4)	N21—C22—C23	119.0 (4)
N11—C12—C17	118.7 (4)	N21—C22—C27	119.6 (4)
C13—C12—C17	122.0 (4)	C23—C22—C27	121.4 (4)
C14—C13—C12	121.5 (4)	C24—C23—C22	121.4 (4)
C14—C13—H13	119.3	C24—C23—H23	119.3
C12—C13—H13	119.3	C22—C23—H23	119.3
C13—C14—C15	117.5 (4)	C23—C24—C25	117.1 (4)
C13—C14—C18	122.3 (4)	C23—C24—C28	121.6 (4)
C15—C14—C18	120.1 (4)	C25—C24—C28	121.3 (4)
C16—C15—C14	119.1 (4)	C26—C25—C24	120.1 (4)
C16—C15—H15	120.4	C26—C25—H25	119.9
C14—C15—H15	120.4	C24—C25—H25	119.9
N11—C16—C15	122.1 (4)	N21—C26—C25	121.5 (4)
N11—C16—H16	119.0	N21—C26—H26	119.3
C15—C16—H16	119.0	C25—C26—H26	119.3
C12—C17—H17A	109.5	C22—C27—H27A	109.5
C12—C17—H17B	109.5	C22—C27—H27B	109.5
H17A—C17—H17B	109.5	H27A—C27—H27B	109.5
C12—C17—H17C	109.5	C22—C27—H27C	109.5
H17A—C17—H17C	109.5	H27A—C27—H27C	109.5
H17B—C17—H17C	109.5	H27B—C27—H27C	109.5
C14—C18—H18A	109.5	C24—C28—H28A	109.5
C14—C18—H18B	109.5	C24—C28—H28B	109.5
H18A—C18—H18B	109.5	H28A—C28—H28B	109.5
C14—C18—H18C	109.5	C24—C28—H28C	109.5
H18A—C18—H18C	109.5	H28A—C28—H28C	109.5
H18B—C18—H18C	109.5	H28B—C28—H28C	109.5
Br3—Au1—N11—C16	84.7 (3)	Br6—Au2—N21—C22	106.4 (3)
Br2—Au1—N11—C16	-93.7 (3)	Br5—Au2—N21—C22	-76.7 (3)
Br3—Au1—N11—C12	-97.3 (3)	Br6—Au2—N21—C26	-72.5 (3)
Br2—Au1—N11—C12	84.3 (3)	Br5—Au2—N21—C26	104.4 (3)
C16—N11—C12—C13	0.4 (6)	C26—N21—C22—C23	1.2 (6)
Au1—N11—C12—C13	-177.5 (3)	Au2—N21—C22—C23	-177.6 (3)
C16—N11—C12—C17	-179.2 (4)	C26—N21—C22—C27	-179.1 (4)

Au1—N11—C12—C17	2.8 (5)	Au2—N21—C22—C27	2.1 (5)
N11—C12—C13—C14	-0.6 (6)	N21—C22—C23—C24	-1.2 (6)
C17—C12—C13—C14	179.0 (4)	C27—C22—C23—C24	179.1 (4)
C12—C13—C14—C15	0.4 (6)	C22—C23—C24—C25	0.3 (6)
C12—C13—C14—C18	179.4 (4)	C22—C23—C24—C28	179.1 (4)
C13—C14—C15—C16	-0.1 (6)	C23—C24—C25—C26	0.7 (6)
C18—C14—C15—C16	-179.1 (4)	C28—C24—C25—C26	-178.2 (4)
C12—N11—C16—C15	-0.1 (6)	C22—N21—C26—C25	-0.3 (6)
Au1—N11—C16—C15	178.0 (3)	Au2—N21—C26—C25	178.6 (3)
C14—C15—C16—N11	-0.1 (7)	C24—C25—C26—N21	-0.7 (7)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C16—H16...Br2 ⁱ	0.95	2.86	3.755 (5)	158
C17—H17C...Br4	0.98	2.89	3.861 (5)	171
C23—H23...Br4 ⁱⁱ	0.95	2.95	3.765 (4)	145
C25—H25...Br2 ⁱⁱⁱ	0.95	2.92	3.851 (4)	166
C26—H26...Br5 ^{iv}	0.95	2.98	3.890 (4)	161
C27—H27B...Br3 ⁱⁱ	0.98	3.07	3.855 (4)	138
C27—H27C...Br5	0.98	3.01	3.647 (4)	124

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x, -y+3/2, z+1/2$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x, -y+1, -z+1$.

Trichlorido(3,5-dimethylpyridine- κ N)gold(III) (5)*Crystal data*

[AuCl₃(C₇H₉N)]

$M_r = 410.47$

Monoclinic, *C*2/*c*

$a = 7.6240$ (3) Å

$b = 15.9360$ (6) Å

$c = 9.2538$ (4) Å

$\beta = 112.333$ (5)°

$V = 1039.97$ (8) Å³

$Z = 4$

$F(000) = 752$

$D_x = 2.622$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6320 reflections

$\theta = 3.2$ – 30.3 °

$\mu = 14.86$ mm⁻¹

$T = 100$ K

Block, yellow

$0.20 \times 0.12 \times 0.04$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1419 pixels mm⁻¹

ω scan

Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2020)

$T_{\min} = 0.270$, $T_{\max} = 1.000$

13810 measured reflections

1563 independent reflections

1496 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 30.9$ °, $\theta_{\min} = 2.6$ °

$h = -10 \rightarrow 10$

$k = -22 \rightarrow 22$

$l = -13 \rightarrow 13$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.014$ $wR(F^2) = 0.032$ $S = 1.07$

1563 reflections

58 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0144P)^2 + 1.5857P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.002$ $\Delta\rho_{\max} = 1.26 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.88 \text{ e } \text{\AA}^{-3}$ *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.500000	0.51448 (2)	0.750000	0.01045 (4)
Cl1	0.500000	0.37193 (5)	0.750000	0.01757 (16)
Cl2	0.74832 (9)	0.51503 (3)	0.66883 (7)	0.01690 (12)
N11	0.500000	0.64233 (17)	0.750000	0.0120 (5)
C12	0.4966 (3)	0.68410 (14)	0.6218 (3)	0.0131 (4)
H12	0.493575	0.653448	0.532835	0.016*
C13	0.4975 (3)	0.77107 (15)	0.6184 (3)	0.0148 (4)
C14	0.500000	0.8142 (2)	0.750000	0.0152 (6)
H14	0.500001	0.873853	0.750001	0.018*
C17	0.4978 (4)	0.81692 (16)	0.4755 (3)	0.0205 (5)
H17A	0.626920	0.818020	0.476847	0.031*
H17B	0.452929	0.874520	0.475849	0.031*
H17C	0.413758	0.787938	0.381216	0.031*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.01446 (7)	0.00766 (7)	0.00989 (6)	0.000	0.00535 (5)	0.000
Cl1	0.0311 (5)	0.0091 (3)	0.0146 (4)	0.000	0.0111 (3)	0.000
Cl2	0.0189 (3)	0.0140 (3)	0.0222 (3)	0.00270 (19)	0.0128 (2)	0.0012 (2)
N11	0.0134 (13)	0.0101 (13)	0.0117 (13)	0.000	0.0039 (10)	0.000
C12	0.0157 (11)	0.0121 (10)	0.0121 (10)	-0.0004 (8)	0.0061 (9)	0.0006 (8)
C13	0.0134 (11)	0.0137 (11)	0.0174 (11)	0.0006 (8)	0.0061 (9)	0.0044 (9)
C14	0.0129 (15)	0.0099 (14)	0.0210 (17)	0.000	0.0046 (13)	0.000
C17	0.0239 (13)	0.0167 (12)	0.0218 (13)	0.0003 (9)	0.0098 (11)	0.0053 (10)

Geometric parameters (\AA , $^\circ$)

Au1—N11	2.037 (3)	C12—H12	0.9500
Au1—Cl1	2.2716 (8)	C13—C14	1.392 (3)
Au1—Cl2	2.2867 (6)	C13—C17	1.512 (3)
Au1—Cl2 ⁱ	2.2867 (6)	C14—H14	0.9500
N11—C12	1.352 (3)	C17—H17A	0.9800
N11—C12 ⁱ	1.352 (3)	C17—H17B	0.9800

C12—C13	1.386 (3)	C17—H17C	0.9800
N11—Au1—C11	180.0	C12—C13—C14	118.2 (2)
N11—Au1—C12	89.779 (14)	C12—C13—C17	120.3 (2)
C11—Au1—C12	90.221 (14)	C14—C13—C17	121.5 (2)
N11—Au1—C12 ⁱ	89.779 (14)	C13—C14—C13 ⁱ	120.8 (3)
C11—Au1—C12 ⁱ	90.221 (14)	C13—C14—H14	119.6
C12—Au1—C12 ⁱ	179.56 (3)	C13 ⁱ —C14—H14	119.6
C12—N11—C12 ⁱ	121.0 (3)	C13—C17—H17A	109.5
C12—N11—Au1	119.50 (14)	C13—C17—H17B	109.5
C12 ⁱ —N11—Au1	119.50 (14)	H17A—C17—H17B	109.5
N11—C12—C13	120.9 (2)	C13—C17—H17C	109.5
N11—C12—H12	119.6	H17A—C17—H17C	109.5
C13—C12—H12	119.6	H17B—C17—H17C	109.5
C12—Au1—N11—C12	51.15 (11)	Au1—N11—C12—C13	-179.68 (16)
C12 ⁱ —Au1—N11—C12	-128.85 (11)	N11—C12—C13—C14	-0.6 (3)
C12—Au1—N11—C12 ⁱ	-128.85 (11)	N11—C12—C13—C17	178.70 (19)
C12 ⁱ —Au1—N11—C12 ⁱ	51.15 (11)	C12—C13—C14—C13 ⁱ	0.31 (15)
C12 ⁱ —N11—C12—C13	0.32 (16)	C17—C13—C14—C13 ⁱ	-179.0 (3)

Symmetry code: (i) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C12—H12···C11 ⁱⁱ	0.95	2.67	3.564 (2)	158
C17—H17C···C11 ⁱⁱ	0.98	3.00	3.666 (3)	126
C14—H14···C12 ⁱⁱⁱ	0.95	2.87	3.659 (3)	142
C14—H14···C12 ^{iv}	0.95	2.87	3.659 (3)	142

Symmetry codes: (ii) $-x+1, -y+1, -z+1$; (iii) $x-1/2, y+1/2, z$; (iv) $-x+3/2, y+1/2, -z+3/2$.

Tribromido(3,5-dimethylpyridine- κ N)gold(III) (6)

Crystal data

[AuBr₃(C₇H₉N)]

$M_r = 543.85$

Triclinic, $P\bar{1}$

$a = 8.2506$ (3) Å

$b = 8.4726$ (4) Å

$c = 9.4210$ (4) Å

$\alpha = 113.828$ (4)°

$\beta = 103.543$ (4)°

$\gamma = 98.368$ (4)°

$V = 563.93$ (5) Å³

$Z = 2$

$F(000) = 484$

$D_x = 3.203$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9505 reflections

$\theta = 2.5$ – 30.5 °

$\mu = 23.62$ mm⁻¹

$T = 100$ K

Plate, red

$0.21 \times 0.15 \times 0.02$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1419 pixels mm⁻¹

ω scan

Absorption correction: analytical
(CrysAlisPro; Rigaku OD, 2020)
 $T_{\min} = 0.050$, $T_{\max} = 0.683$
30785 measured reflections
3392 independent reflections
3017 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.071$
 $\theta_{\max} = 31.1^\circ$, $\theta_{\min} = 2.5^\circ$
 $h = -11 \rightarrow 11$
 $k = -12 \rightarrow 11$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.059$
 $S = 1.06$
3392 reflections
111 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 1.2689P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.61 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.50 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Au1	0.12370 (2)	0.25661 (2)	0.49051 (2)	0.01349 (6)	
Br1	0.03437 (6)	0.14810 (6)	0.19990 (6)	0.01893 (10)	
Br2	0.40986 (6)	0.22579 (7)	0.48839 (6)	0.02386 (11)	
Br3	-0.16592 (6)	0.28402 (6)	0.48783 (6)	0.01976 (10)	
N11	0.2017 (4)	0.3438 (5)	0.7424 (5)	0.0147 (7)	
C12	0.2688 (6)	0.2381 (6)	0.8004 (6)	0.0168 (9)	
H12	0.279048	0.126752	0.726372	0.020*	
C13	0.3231 (5)	0.2900 (6)	0.9669 (6)	0.0158 (9)	
C14	0.3052 (6)	0.4523 (6)	1.0705 (6)	0.0190 (9)	
H14	0.340733	0.489516	1.185204	0.023*	
C15	0.2367 (6)	0.5623 (6)	1.0112 (6)	0.0151 (8)	
C16	0.1850 (6)	0.5024 (6)	0.8425 (6)	0.0166 (9)	
H16	0.137385	0.574253	0.797647	0.020*	
C17	0.4003 (6)	0.1710 (7)	1.0302 (6)	0.0214 (10)	
H17A	0.521624	0.232331	1.097981	0.032*	
H17B	0.394076	0.059044	0.937453	0.032*	
H17C	0.335545	0.144135	1.096319	0.032*	
C18	0.2204 (7)	0.7414 (6)	1.1209 (6)	0.0214 (10)	
H18A	0.124462	0.770022	1.061149	0.032*	0.5
H18B	0.328297	0.833284	1.156030	0.032*	0.5
H18C	0.197840	0.737961	1.217411	0.032*	0.5
H18D	0.309270	0.790823	1.228578	0.032*	0.5
H18E	0.105436	0.727561	1.133697	0.032*	0.5

H18F	0.235893	0.822884	1.072316	0.032*	0.5
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Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.01095 (9)	0.01390 (9)	0.01380 (9)	0.00301 (6)	0.00348 (6)	0.00499 (7)
Br1	0.0185 (2)	0.0214 (2)	0.0142 (2)	0.00721 (18)	0.00391 (17)	0.00575 (18)
Br2	0.0129 (2)	0.0346 (3)	0.0185 (2)	0.00827 (19)	0.00475 (18)	0.0063 (2)
Br3	0.0126 (2)	0.0245 (2)	0.0206 (2)	0.00569 (18)	0.00643 (18)	0.00792 (19)
N11	0.0085 (16)	0.0160 (18)	0.021 (2)	0.0032 (14)	0.0021 (15)	0.0115 (16)
C12	0.015 (2)	0.011 (2)	0.024 (2)	0.0024 (16)	0.0077 (18)	0.0066 (18)
C13	0.0098 (19)	0.017 (2)	0.020 (2)	-0.0006 (16)	0.0028 (17)	0.0105 (19)
C14	0.015 (2)	0.017 (2)	0.022 (2)	-0.0005 (18)	0.0044 (19)	0.0083 (19)
C15	0.016 (2)	0.012 (2)	0.017 (2)	0.0020 (16)	0.0054 (17)	0.0065 (17)
C16	0.015 (2)	0.013 (2)	0.022 (2)	0.0036 (17)	0.0055 (18)	0.0085 (18)
C17	0.019 (2)	0.024 (3)	0.029 (3)	0.008 (2)	0.007 (2)	0.019 (2)
C18	0.028 (3)	0.021 (2)	0.016 (2)	0.007 (2)	0.008 (2)	0.0075 (19)

Geometric parameters (Å, °)

Au1—N11	2.078 (4)	C15—C16	1.391 (6)
Au1—Br1	2.3892 (5)	C15—C18	1.499 (6)
Au1—Br2	2.4167 (5)	C16—H16	0.9500
Au1—Br3	2.4295 (4)	C17—H17A	0.9800
N11—C16	1.344 (6)	C17—H17B	0.9800
N11—C12	1.344 (6)	C17—H17C	0.9800
C12—C13	1.382 (7)	C18—H18A	0.9800
C12—H12	0.9500	C18—H18B	0.9800
C13—C14	1.381 (6)	C18—H18C	0.9800
C13—C17	1.508 (6)	C18—H18D	0.9800
C14—C15	1.388 (6)	C18—H18E	0.9800
C14—H14	0.9500	C18—H18F	0.9800
N11—Au1—Br1	178.39 (10)	H17A—C17—H17B	109.5
N11—Au1—Br2	90.03 (10)	C13—C17—H17C	109.5
Br1—Au1—Br2	89.437 (17)	H17A—C17—H17C	109.5
N11—Au1—Br3	90.85 (10)	H17B—C17—H17C	109.5
Br1—Au1—Br3	89.674 (17)	C15—C18—H18A	109.5
Br2—Au1—Br3	179.045 (17)	C15—C18—H18B	109.5
C16—N11—C12	121.8 (4)	H18A—C18—H18B	109.5
C16—N11—Au1	120.0 (3)	C15—C18—H18C	109.5
C12—N11—Au1	118.2 (3)	H18A—C18—H18C	109.5
N11—C12—C13	120.5 (4)	H18B—C18—H18C	109.5
N11—C12—H12	119.7	C15—C18—H18D	109.5
C13—C12—H12	119.7	H18A—C18—H18D	141.1
C14—C13—C12	118.0 (4)	H18B—C18—H18D	56.3
C14—C13—C17	122.1 (4)	H18C—C18—H18D	56.3
C12—C13—C17	119.9 (4)	C15—C18—H18E	109.5

C13—C14—C15	121.6 (5)	H18A—C18—H18E	56.3
C13—C14—H14	119.2	H18B—C18—H18E	141.1
C15—C14—H14	119.2	H18C—C18—H18E	56.3
C14—C15—C16	117.5 (4)	H18D—C18—H18E	109.5
C14—C15—C18	122.9 (4)	C15—C18—H18F	109.5
C16—C15—C18	119.7 (4)	H18A—C18—H18F	56.3
N11—C16—C15	120.5 (4)	H18B—C18—H18F	56.3
N11—C16—H16	119.7	H18C—C18—H18F	141.1
C15—C16—H16	119.7	H18D—C18—H18F	109.5
C13—C17—H17A	109.5	H18E—C18—H18F	109.5
C13—C17—H17B	109.5		
Br2—Au1—N11—C16	124.0 (3)	C12—C13—C14—C15	-0.6 (7)
Br3—Au1—N11—C16	-56.3 (3)	C17—C13—C14—C15	178.9 (4)
Br2—Au1—N11—C12	-55.8 (3)	C13—C14—C15—C16	0.5 (6)
Br3—Au1—N11—C12	123.9 (3)	C13—C14—C15—C18	-178.2 (4)
C16—N11—C12—C13	0.1 (6)	C12—N11—C16—C15	-0.2 (6)
Au1—N11—C12—C13	179.9 (3)	Au1—N11—C16—C15	180.0 (3)
N11—C12—C13—C14	0.4 (6)	C14—C15—C16—N11	-0.1 (6)
N11—C12—C13—C17	-179.2 (4)	C18—C15—C16—N11	178.7 (4)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C16—H16 \cdots Br1 ⁱ	0.95	2.91	3.792 (4)	154
C17—H17C \cdots Br1 ⁱⁱ	0.98	2.87	3.749 (5)	149
C18—H18A \cdots Br1 ⁱ	0.98	2.89	3.784 (5)	151
C18—H18C \cdots Br3 ⁱⁱⁱ	0.98	2.93	3.902 (5)	174
C14—H14 \cdots Br2 ^{iv}	0.95	3.02	3.826 (5)	144

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x, y, z+1$; (iii) $-x, -y+1, -z+2$; (iv) $-x+1, -y+1, -z+2$.Trichlorido(2,6-dimethylpyridine- κ N)gold(III) (7)

Crystal data

[AuCl₃(C₇H₉N)] $M_r = 410.47$ Monoclinic, $C2/c$ $a = 11.0184$ (3) \AA $b = 10.6600$ (2) \AA $c = 9.7760$ (3) \AA $\beta = 113.053$ (3) $^\circ$ $V = 1056.55$ (5) \AA^3 $Z = 4$ $F(000) = 752$ $D_x = 2.580$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 11513 reflections

 $\theta = 2.8\text{--}30.8^\circ$ $\mu = 14.63$ mm⁻¹ $T = 100$ K

Block, yellow

 $0.22 \times 0.20 \times 0.12$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1419 pixels mm⁻¹ ω scan

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2020)

 $T_{\min} = 0.267$, $T_{\max} = 1.000$

15246 measured reflections

1600 independent reflections
 1553 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 31.1^\circ$, $\theta_{\text{min}} = 2.8^\circ$

$h = -15 \rightarrow 15$
 $k = -15 \rightarrow 15$
 $l = -14 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.013$
 $wR(F^2) = 0.026$
 $S = 1.12$
 1600 reflections
 59 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.008P)^2 + 2.0823P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.83 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.17 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL-2019/3
 (Sheldrick, 2015),
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00079 (4)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.500000	0.07715 (2)	0.250000	0.00999 (4)
Cl1	0.500000	-0.13530 (6)	0.250000	0.01876 (14)
Cl2	0.67610 (5)	0.07948 (5)	0.47293 (6)	0.01738 (10)
N11	0.500000	0.2681 (2)	0.250000	0.0116 (4)
C12	0.5772 (2)	0.33032 (19)	0.1927 (2)	0.0134 (4)
C13	0.5773 (2)	0.4602 (2)	0.1918 (2)	0.0188 (4)
H13	0.630269	0.504531	0.151332	0.023*
C14	0.500000	0.5250 (3)	0.250000	0.0209 (7)
H14	0.500000	0.614152	0.249999	0.025*
C17	0.6610 (2)	0.2555 (2)	0.1346 (3)	0.0209 (4)
H17A	0.728384	0.210384	0.216707	0.031*
H17B	0.703983	0.311872	0.087995	0.031*
H17C	0.605857	0.195208	0.060762	0.031*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.00944 (6)	0.00806 (5)	0.01165 (6)	0.000	0.00326 (4)	0.000
Cl1	0.0217 (4)	0.0089 (3)	0.0221 (4)	0.000	0.0047 (3)	0.000
Cl2	0.0149 (2)	0.0166 (2)	0.0153 (2)	0.00108 (17)	0.00006 (19)	-0.00011 (17)
N11	0.0128 (11)	0.0086 (10)	0.0119 (10)	0.000	0.0031 (9)	0.000
C12	0.0121 (9)	0.0150 (9)	0.0114 (9)	-0.0026 (7)	0.0028 (8)	-0.0004 (7)
C13	0.0205 (11)	0.0143 (9)	0.0171 (10)	-0.0062 (8)	0.0025 (9)	0.0015 (8)
C14	0.0222 (16)	0.0106 (13)	0.0226 (16)	0.000	0.0011 (13)	0.000
C17	0.0224 (11)	0.0214 (11)	0.0249 (11)	-0.0048 (9)	0.0157 (9)	-0.0040 (9)

Geometric parameters (\AA , $^\circ$)

Au1—N11	2.036 (2)	C12—C17	1.491 (3)
Au1—C11	2.2648 (7)	C13—C14	1.380 (3)
Au1—C12	2.2811 (5)	C13—H13	0.9500
Au1—C12 ⁱ	2.2811 (5)	C14—H14	0.9500
N11—C12 ⁱ	1.360 (2)	C17—H17A	0.9800
N11—C12	1.360 (2)	C17—H17B	0.9800
C12—C13	1.385 (3)	C17—H17C	0.9800
N11—Au1—C11	180.0	C14—C13—C12	119.8 (2)
N11—Au1—C12	89.375 (12)	C14—C13—H13	120.1
C11—Au1—C12	90.625 (12)	C12—C13—H13	120.1
N11—Au1—C12 ⁱ	89.375 (12)	C13—C14—C13 ⁱ	119.9 (3)
C11—Au1—C12 ⁱ	90.625 (12)	C13—C14—H14	120.1
C12—Au1—C12 ⁱ	178.75 (2)	C13 ⁱ —C14—H14	120.1
C12 ⁱ —N11—C12	121.7 (2)	C12—C17—H17A	109.5
C12 ⁱ —N11—Au1	119.17 (12)	C12—C17—H17B	109.5
C12—N11—Au1	119.16 (12)	H17A—C17—H17B	109.5
N11—C12—C13	119.4 (2)	C12—C17—H17C	109.5
N11—C12—C17	118.50 (18)	H17A—C17—H17C	109.5
C13—C12—C17	122.0 (2)	H17B—C17—H17C	109.5
C12—Au1—N11—C12 ⁱ	−92.76 (10)	C12 ⁱ —N11—C12—C17	178.9 (2)
C12 ⁱ —Au1—N11—C12 ⁱ	87.24 (10)	Au1—N11—C12—C17	−1.1 (2)
C12—Au1—N11—C12	87.24 (10)	N11—C12—C13—C14	0.5 (3)
C12 ⁱ —Au1—N11—C12	−92.76 (10)	C17—C12—C13—C14	−178.59 (17)
C12 ⁱ —N11—C12—C13	−0.27 (15)	C12—C13—C14—C13 ⁱ	−0.27 (15)
Au1—N11—C12—C13	179.73 (15)		

Symmetry code: (i) $-x+1, y, -z+1/2$.Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C17—H17C \cdots C11 ⁱⁱ	0.98	2.87	3.701 (2)	144
C14—H14 \cdots C11 ⁱⁱⁱ	0.95	2.67	3.621 (3)	180

Symmetry codes: (ii) $-x+1, -y, -z$; (iii) $x, y+1, z$.Tribromido(2-methylpyridine- κ N)gold(III)–tribromido(3,5-dimethylpyridine- κ N)gold(III) (8)

Crystal data

[AuBr₃(C₇H₉N)] \cdot [AuBr₃(C₆H₇N)] $M_r = 1073.67$ Triclinic, $P\bar{1}$ $a = 9.1741$ (9) \AA $b = 11.1922$ (9) \AA $c = 11.4596$ (7) \AA $\alpha = 83.990$ (6) $^\circ$ $\beta = 80.777$ (6) $^\circ$ $\gamma = 69.147$ (8) $^\circ$ $V = 1083.92$ (16) \AA^3 $Z = 2$ $F(000) = 952$ $D_x = 3.290$ Mg m^{-3} Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 9704 reflections

 $\theta = 2.4\text{--}28.2^\circ$

$\mu = 24.58 \text{ mm}^{-1}$
 $T = 100 \text{ K}$

Plate, red
 $0.13 \times 0.06 \times 0.02 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur, Eos
 diffractometer
 Radiation source: Enhance (Mo) X-ray Source
 Graphite monochromator
 Detector resolution: 16.1419 pixels mm^{-1}
 ω scans
 Absorption correction: multi-scan
 (CrysAlisPro; Rigaku OD, 2020)
 $T_{\min} = 0.052$, $T_{\max} = 1.000$

7479 measured reflections
 7479 independent reflections
 5015 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = -$
 $\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.4^\circ$
 $h = -12 \rightarrow 12$
 $k = -14 \rightarrow 14$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.055$
 $S = 0.82$
 7479 reflections
 212 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0197P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 2.15 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.91 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.31055 (5)	0.18855 (4)	0.47765 (3)	0.01428 (9)
Au2	0.26051 (4)	0.26264 (4)	0.06975 (3)	0.01319 (9)
Br1	0.12467 (12)	0.08172 (11)	0.48592 (9)	0.0298 (3)
Br2	0.48387 (11)	0.05181 (9)	0.32392 (8)	0.0193 (2)
Br3	0.13402 (12)	0.33442 (10)	0.62169 (9)	0.0229 (2)
Br4	0.44662 (11)	0.37133 (9)	0.03511 (8)	0.0208 (2)
Br5	0.38703 (11)	0.14154 (9)	-0.10337 (8)	0.0235 (3)
Br6	0.13174 (11)	0.38514 (9)	0.24300 (8)	0.0201 (2)
N11	0.4748 (9)	0.2745 (7)	0.4755 (6)	0.0151 (19)
C12	0.5284 (11)	0.3271 (8)	0.3743 (8)	0.019 (2)
H12	0.486387	0.326809	0.303804	0.022*
C13	0.6413 (10)	0.3808 (8)	0.3701 (7)	0.015 (2)
C14	0.7044 (10)	0.3796 (8)	0.4740 (8)	0.017 (2)
H14	0.784577	0.414986	0.473172	0.021*
C15	0.6476 (11)	0.3256 (8)	0.5787 (8)	0.018 (2)
C16	0.5329 (10)	0.2740 (8)	0.5777 (8)	0.017 (2)
H16	0.493571	0.237639	0.648890	0.020*
C17	0.6978 (11)	0.4381 (8)	0.2553 (7)	0.023 (2)
H17A	0.672071	0.530073	0.262125	0.035*
H17B	0.646182	0.424555	0.191795	0.035*
H17C	0.812018	0.396959	0.236885	0.035*
C18	0.7075 (11)	0.3281 (9)	0.6942 (8)	0.028 (3)

H18A	0.661146	0.280832	0.756858	0.042*
H18B	0.677659	0.417031	0.715550	0.042*
H18C	0.822385	0.288205	0.684560	0.042*
N21	0.1008 (9)	0.1688 (7)	0.1000 (6)	0.0181 (19)
C22	-0.0324 (12)	0.2102 (9)	0.0472 (8)	0.024 (3)
C23	-0.1378 (12)	0.1462 (10)	0.0739 (9)	0.027 (3)
H23	-0.229091	0.172514	0.035102	0.032*
C24	-0.1124 (11)	0.0427 (10)	0.1576 (9)	0.027 (3)
H24	-0.186489	0.000153	0.178792	0.032*
C25	0.0248 (12)	0.0055 (9)	0.2077 (8)	0.028 (3)
H25	0.046356	-0.064793	0.264405	0.033*
C26	0.1292 (12)	0.0668 (9)	0.1779 (7)	0.024 (2)
H26	0.224149	0.037801	0.212418	0.028*
C27	-0.0574 (11)	0.3212 (9)	-0.0393 (8)	0.025 (3)
H27A	-0.054252	0.394707	-0.001573	0.037*
H27B	-0.160173	0.342710	-0.066478	0.037*
H27C	0.025593	0.299627	-0.107068	0.037*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.0161 (2)	0.0168 (2)	0.01202 (19)	-0.00802 (17)	-0.00045 (15)	-0.00383 (15)
Au2	0.0150 (2)	0.0127 (2)	0.01178 (19)	-0.00456 (17)	-0.00136 (15)	-0.00158 (15)
Br1	0.0368 (7)	0.0457 (8)	0.0205 (6)	-0.0322 (6)	0.0043 (4)	-0.0086 (5)
Br2	0.0224 (5)	0.0190 (6)	0.0171 (5)	-0.0080 (4)	0.0021 (4)	-0.0074 (4)
Br3	0.0177 (5)	0.0311 (6)	0.0204 (5)	-0.0085 (5)	0.0045 (4)	-0.0138 (4)
Br4	0.0217 (6)	0.0206 (6)	0.0231 (5)	-0.0116 (5)	-0.0017 (4)	-0.0008 (4)
Br5	0.0271 (6)	0.0279 (6)	0.0173 (5)	-0.0121 (5)	0.0043 (4)	-0.0100 (5)
Br6	0.0213 (5)	0.0192 (5)	0.0189 (5)	-0.0057 (4)	0.0006 (4)	-0.0068 (4)
N11	0.012 (4)	0.014 (4)	0.021 (4)	-0.005 (4)	-0.001 (4)	-0.009 (3)
C12	0.018 (5)	0.012 (5)	0.019 (5)	0.002 (4)	-0.001 (4)	-0.007 (4)
C13	0.013 (5)	0.010 (5)	0.018 (5)	0.000 (4)	0.002 (4)	-0.007 (4)
C14	0.013 (5)	0.016 (5)	0.024 (5)	-0.004 (4)	-0.001 (4)	-0.008 (4)
C15	0.014 (5)	0.015 (5)	0.022 (5)	-0.001 (4)	-0.007 (4)	0.001 (4)
C16	0.018 (5)	0.018 (5)	0.013 (5)	-0.006 (4)	-0.003 (4)	0.000 (4)
C17	0.033 (6)	0.021 (6)	0.022 (5)	-0.015 (5)	-0.001 (4)	-0.010 (4)
C18	0.021 (6)	0.034 (6)	0.036 (6)	-0.016 (5)	-0.017 (5)	0.013 (5)
N21	0.019 (5)	0.017 (5)	0.013 (4)	-0.001 (4)	0.002 (3)	-0.003 (3)
C22	0.024 (6)	0.023 (6)	0.018 (5)	0.005 (5)	-0.006 (5)	-0.013 (5)
C23	0.014 (5)	0.035 (7)	0.031 (6)	-0.006 (5)	0.004 (5)	-0.019 (5)
C24	0.018 (6)	0.030 (7)	0.035 (6)	-0.012 (5)	0.013 (5)	-0.025 (5)
C25	0.036 (7)	0.023 (6)	0.026 (6)	-0.015 (5)	0.003 (5)	-0.002 (5)
C26	0.032 (6)	0.029 (6)	0.008 (5)	-0.008 (5)	-0.003 (4)	-0.001 (4)
C27	0.023 (6)	0.029 (6)	0.019 (5)	-0.002 (5)	-0.007 (4)	-0.003 (4)

Geometric parameters (Å, °)

Au1—N11	2.053 (8)	C17—H17B	0.9800
Au1—Br1	2.3922 (11)	C17—H17C	0.9800
Au1—Br3	2.4162 (9)	C18—H18A	0.9800
Au1—Br2	2.4306 (10)	C18—H18B	0.9800
Au2—N21	2.056 (8)	C18—H18C	0.9800
Au2—Br4	2.3901 (11)	N21—C26	1.348 (11)
Au2—Br5	2.4136 (9)	N21—C22	1.360 (11)
Au2—Br6	2.4253 (10)	C22—C23	1.376 (14)
N11—C12	1.347 (11)	C22—C27	1.480 (12)
N11—C16	1.360 (10)	C23—C24	1.400 (13)
C12—C13	1.362 (12)	C23—H23	0.9500
C12—H12	0.9500	C24—C25	1.377 (13)
C13—C14	1.402 (11)	C24—H24	0.9500
C13—C17	1.501 (12)	C25—C26	1.349 (13)
C14—C15	1.395 (12)	C25—H25	0.9500
C14—H14	0.9500	C26—H26	0.9500
C15—C16	1.371 (12)	C27—H27A	0.9800
C15—C18	1.519 (11)	C27—H27B	0.9800
C16—H16	0.9500	C27—H27C	0.9800
C17—H17A	0.9800		
N11—Au1—Br1	177.6 (2)	C13—C17—H17C	109.5
N11—Au1—Br3	90.3 (2)	H17A—C17—H17C	109.5
Br1—Au1—Br3	90.02 (4)	H17B—C17—H17C	109.5
N11—Au1—Br2	89.0 (2)	C15—C18—H18A	109.5
Br1—Au1—Br2	90.84 (4)	C15—C18—H18B	109.5
Br3—Au1—Br2	176.66 (4)	H18A—C18—H18B	109.5
N21—Au2—Br4	179.8 (2)	C15—C18—H18C	109.5
N21—Au2—Br5	89.90 (19)	H18A—C18—H18C	109.5
Br4—Au2—Br5	90.14 (4)	H18B—C18—H18C	109.5
N21—Au2—Br6	89.95 (19)	C26—N21—C22	120.6 (9)
Br4—Au2—Br6	90.01 (4)	C26—N21—Au2	117.7 (7)
Br5—Au2—Br6	179.59 (4)	C22—N21—Au2	121.6 (7)
C12—N11—C16	120.2 (9)	N21—C22—C23	119.1 (9)
C12—N11—Au1	120.9 (6)	N21—C22—C27	118.7 (10)
C16—N11—Au1	118.8 (6)	C23—C22—C27	122.2 (9)
N11—C12—C13	121.9 (9)	C22—C23—C24	120.9 (9)
N11—C12—H12	119.1	C22—C23—H23	119.5
C13—C12—H12	119.1	C24—C23—H23	119.5
C12—C13—C14	118.9 (9)	C25—C24—C23	117.1 (10)
C12—C13—C17	120.0 (8)	C25—C24—H24	121.5
C14—C13—C17	121.1 (9)	C23—C24—H24	121.5
C15—C14—C13	119.0 (9)	C26—C25—C24	121.2 (10)
C15—C14—H14	120.5	C26—C25—H25	119.4
C13—C14—H14	120.5	C24—C25—H25	119.4
C16—C15—C14	119.6 (8)	N21—C26—C25	121.0 (9)

C16—C15—C18	119.9 (9)	N21—C26—H26	119.5
C14—C15—C18	120.5 (9)	C25—C26—H26	119.5
N11—C16—C15	120.5 (9)	C22—C27—H27A	109.5
N11—C16—H16	119.7	C22—C27—H27B	109.5
C15—C16—H16	119.7	H27A—C27—H27B	109.5
C13—C17—H17A	109.5	C22—C27—H27C	109.5
C13—C17—H17B	109.5	H27A—C27—H27C	109.5
H17A—C17—H17B	109.5	H27B—C27—H27C	109.5
Br3—Au1—N11—C12	-121.6 (6)	Br5—Au2—N21—C26	96.6 (6)
Br2—Au1—N11—C12	55.2 (6)	Br6—Au2—N21—C26	-83.8 (6)
Br3—Au1—N11—C16	60.5 (6)	Br5—Au2—N21—C22	-86.0 (7)
Br2—Au1—N11—C16	-122.7 (6)	Br6—Au2—N21—C22	93.7 (7)
C16—N11—C12—C13	0.1 (12)	C26—N21—C22—C23	-0.4 (14)
Au1—N11—C12—C13	-177.7 (6)	Au2—N21—C22—C23	-177.7 (6)
N11—C12—C13—C14	0.8 (13)	C26—N21—C22—C27	-179.0 (8)
N11—C12—C13—C17	179.9 (7)	Au2—N21—C22—C27	3.6 (12)
C12—C13—C14—C15	-1.1 (12)	N21—C22—C23—C24	2.4 (14)
C17—C13—C14—C15	179.8 (8)	C27—C22—C23—C24	-178.9 (9)
C13—C14—C15—C16	0.6 (13)	C22—C23—C24—C25	-2.5 (14)
C13—C14—C15—C18	-177.1 (8)	C23—C24—C25—C26	0.5 (15)
C12—N11—C16—C15	-0.7 (12)	C22—N21—C26—C25	-1.6 (14)
Au1—N11—C16—C15	177.2 (6)	Au2—N21—C26—C25	175.8 (7)
C14—C15—C16—N11	0.3 (13)	C24—C25—C26—N21	1.6 (15)
C18—C15—C16—N11	178.1 (8)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C18—H18C \cdots Br3 ⁱ	0.98	3.05	3.892 (10)	145
C23—H23 \cdots Br4 ⁱⁱ	0.95	3.01	3.815 (10)	143
C17—H17C \cdots Br6 ⁱ	0.98	2.90	3.792 (10)	152
C12—H12 \cdots Br4	0.95	3.13	4.023 (9)	158
C16—H16 \cdots Br5 ⁱⁱⁱ	0.95	3.06	4.007 (9)	172
C25—H25 \cdots Br1 ^{iv}	0.95	3.06	3.721 (10)	128
C26—H26 \cdots Br2	0.95	2.94	3.835 (10)	159
C27—H27C \cdots Br3 ^v	0.98	3.14	4.010 (9)	149

Symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z$; (iii) $x, y, z+1$; (iv) $-x, -y, -z+1$; (v) $x, y, z-1$.