Hydrogen bonds C–H···Cl as a structure-determining factor in the gold(I) complex bis(3-bromopyridine)gold(I) dichloroaurate(I)†

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The crystal structure of the title compound involves three types of secondary interaction; hydrogen bonds of the form C–H···Cl account for the mutually perpendicular arrangement of the cations and anions.

We are interested in gold(I) complexes with amine ligands and have recently reported the synthesis and structure of such complexes with aliphatic amines[1] and with pyridines.[2] Our other current studies involve the investigation of intermolecular contacts such as hydrogen bonds (including non-classical cases such as C–H···X), aurophilic interactions,[3] and halogen–halogen contacts.[4] These fields naturally overlap, and we have established the importance of classical hydrogen bonds in gold(I) amine complexes,[1] and of C–H···Cl contacts in some gold(I) dppm complexes.[5]

Here, we present the structure of bis(3-bromopyridine)gold(I) dichloroaurate(I) **1**.‡ The compound was obtained from 3-bromopyridine and tetrahydrothiophene(chloro)gold(I).§ As will be seen below, the primary structure is unexceptional but the secondary interactions extensive and varied.

The structure analysis shows that compound **1** crystallizes in the ionic form $(L_2Au)^+(AuCl_2)^-$ (L = pyridine ligand); in principle, such complexes can also display the alternative molecular form LAuCl. The balance between the two forms is very sensitive, as can be seen from the fact that the 2-picoline derivative is molecular but the 3-picoline derivative ionic.[2] The non-substituted bis(pyridine)gold(I) dichloroaurate(I) also displays the ionic form.[6]

The asymmetric unit of **1** consists of one cation and one anion, each without imposed crystallographic symmetry. In both ions the geometry at the gold centre is, as expected, linear, with normal dimensions Au1–N 2.009(10), 2.035(10) Å, N–Au1–N 173.8(4)°, Au2–Cl 2.259(3), 2.267(3) Å, Cl–Au(2)–Cl 177.61(12)°. The bromo substituents, like the methyl substituents of the 3-picoline analogue (which displays strict inversion symmetry)[2] are *trans* to each other.

The extended structure of **1** involves three distinct kinds of secondary interaction: *aurophilic interactions*,[3] C–H···Cl *hydrogen bonds* and Br···Cl *interhalogen contacts*. It is well known that gold(I) centres have a marked tendency to aggregation. In **1**, short aurophilic contacts are observed both within the asymmetric unit [Au1···Au2 3.2681(7) Å], and *via* the inversion operator $1 - x, 1 - y, 1 - z$ [Au1···Au1# 3.3113(10) Å]. The ions are thereby connected to form 'isolated' (see below!) dimeric units containing a zigzag chain of four gold atoms (Fig. 2), similar to the complex bis(pyridine)gold(I) dichloroaurate(I).[6] In the 3-picoline complex, Au···Au contacts lead to infinite zigzag chains with alternating cations and anions.[2] In all three structures, the L–Au–L axes of cation and anion are approximately perpendicular to each other; a typical torsion angle in **1** is N1′–Au1–Au2–Cl2 −90.1(3°).

A more detailed inspection shows that the extended structure of **1** is not solely characterised by aurophilic contacts. Within the dimeric unit (Fig. 1) there are eight (four independent) C–H···Cl contacts (Table 1, first four entries), formed *via* the H atoms *ortho* to nitrogen. These may reasonably be considered as C–H···Cl hydrogen bonds,[7] since they are essentially linear, with H···Cl distances appreciably less than the sum of the van der Waals radii (2.95 Å); they are *charge-assisted*[8] by the opposite charges of anion and cation.. The corresponding H···Cl–Au angles lie in the range 72–85°. Although steric factors must also play a role, the formation of such hydrogen bonds provides a good explanation for the mutually perpendicular orientation of anions and cations. As far as we are aware, this is the first time that C–H···Cl interactions have been explicitly cited as conformation-determining factors in metal complexes.[9] The presence of a 2-methyl group in the 2-picoline derivative blocks one of the potential hydrogen bonding sites, which may be one reason why a non-ionic structure is preferred.[2] Inspection of the bis(pyridine)gold(I) dichloroaurate(I) structure[6] shows an exactly analogous framework to that of **1**. The 3-picoline derivative[2] exhibits two C–H···Cl contacts within

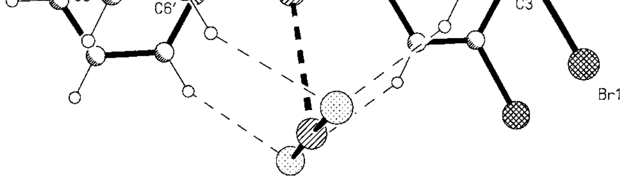

Fig. 1 Dimeric unit of **1** in the crystal. Radii are arbitrary. Only the asymmetric unit is numbered. Gold···gold contacts are represented by thick dashed lines, C–H···Cl contacts as thin dashed lines.

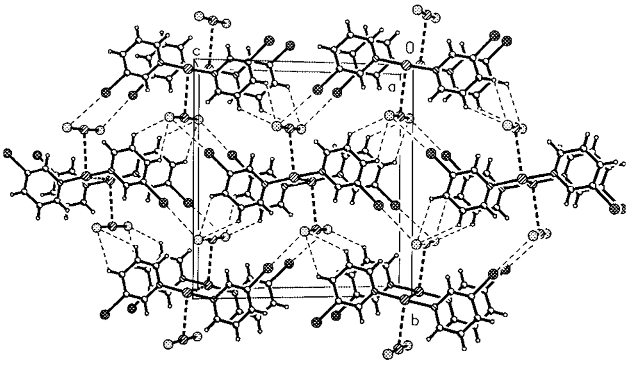

Fig. 2 Packing diagram of **1** parallel to the *x* axis. Gold···gold contacts are represented by thick dashed lines, C–H···Cl and Br···Cl contacts as thin dashed lines. C–H···Cl contacts within the dimeric units are omitted.

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† Gold complexes with amine ligands, Part 5.[1]

Table 1 Geometrical data (Å, °) for the hydrogen bonds and interhalogen contacts in **1**[a]

System	*d*(H···Cl)[10]	∠(CH···Cl)	∠(H···Cl–Au2)
C2′–H2′···Cl1	2.69	151	72
C2–H2···Cl2#1	2.69	144	85
C6′–H6′···Cl2#1	2.62	144	80
C6–H6···Cl1	2.55	155	75
C4′–H4′···Cl2#2	2.92	120	92
C4–H4···Cl1#3	2.91	118	80
C5′–H5′···Cl2#2	2.87	123	75
C5–H5···Cl1#3	2.71	127	93

System	*d*(Br···Cl)	∠(CBr···Cl)
C3–Br1···Cl2#2	3.384(3)	169.6(4)
C3′–Br1′···Cl1#4	3.441(4)	173.1(4)

[a] Symmetry transformations: #1 1 − *x*,1 − *y*,1 − *z*; #2 1.5 − *x*,0.5 + *y*,1.5 − *z*; #3 −0.5 + *x*,0.5 − *y*, − 0.5 + *z*; #4 0.5 + *x*,0.5 − *y*,0.5 + *z*.

the chain and one between chains, with H···Cl 2.59, 2.84, 2.72 Å respectively;[10] regrettably, this did not attract our attention at the time.

An analysis of the packing of the dimeric units reveals further secondary interactions between the dimeric units. The packing diagram parallel to the *x* axis shows a layer structure (Fig. 2) with additional, slightly longer and less linear C–H···Cl contacts, leading to five-membered rings C4–H4···Cl···H5–C5 (Table 1, entries 5–8). Finally, there are Br···Cl contacts of 3.441(4) (Br1′···Cl1) and 3.384(3) Å (Br1···Cl2). These lie well below the sum of the van der Waals radii (3.6 Å), and the angles C3′–Br1′···Cl1 and C3-Br1···Cl2 [173.1(4) and 169.6(4)°] are essentially linear; thus these contacts may be classed as charge-assisted electrostatic interactions of the form $Br^{\delta+}\cdots Cl^{\delta-}$ (*cf.* analogous Cl···O [11] or Cl···Cl [4] contacts).

We conclude that non-conventional hydrogen bonds may play an important role in determining the structure of metal complexes. Furthermore, in view of the increasing interest in secondary interactions, great caution is needed in describing crystal packing in terms of *isolated* molecules or ions!

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Notes and references

‡ *X-Ray structure analysis*: *Crystal data*: $C_{10}H_8Au_2Br_2Cl_2N_2$, monoclinic, space group $P2_1/n$, a = 7.5360(8), b = 14.4660(14), c = 14.0832(12) Å, β = 101.951(8)°, V = 1502.0(3) Å^3, Z = 4, μ(Mo-Kα) = 25.2 mm^{-1}, T = −100 °C. *Data collection*: colourless prism 0.45 × 0.10 × 0.06 mm, Siemens P4 diffractometer; absorption correction based on ψ-scans (transmissions 0.41–0.99). Measured reflections 3122 ($2\theta_{max}$ 50°), 2636 independent (R_{int} 0.053). *Structure solution and refinement*: heavy atom method, anisotropic refinement on F^2 (SHELXL-97, G. M. Sheldrick, University of Göttingen). Hydrogen atoms included using a riding model. Final $wR2$ 0.087, with $R1$ 0.037, for 163 parameters; S 0.91; max. $\Delta\rho$ 2.8 e Å^{-3}.

CCDC 182/1526. See http://www.rsc.org/suppdata/cc/a9/a907523b/ for crystallographic files in .cif format.

§ *Preparation* of **1**: To 2 ml (10 mmol) 3-bromopyridine were added 0.5 g (1.5 mmol) tetrahydrothiophene(chloro)gold(I). After 1 h stirring, the solution was transferred to small crystallisation tubes and left in the dark for 10 days. Small colourless crystals of **1** were formed in low yield, together with metallic gold. The quantity was insufficient for elemental analysis or spectroscopic studies. No product could be isolated from analogous reactions with other halogenated pyridines.

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