4,4′-Bi(1H-pyrazol-2-ium) tetrachloridoaurate(III) chloride: a three-dimensional cationic cooperite-like framework with multiple pyrazolium–chloride hydrogen-bonding interactions

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In the title compound, $(C_6H_8N_4)[AuCl_4]Cl$, the 4,4′-bi(1H-pyrazol-2-ium) dication, denoted $[H_2bpz]^{2+}$, is situated across a centre of inversion, the $[AuCl_4]^-$ anion lies across a twofold axis passing through Cl—Au—Cl, and the Cl^- anion resides on a twofold axis. Conventional N—H···Cl hydrogen bonding [N···Cl = 3.109 (3) and 3.127 (3) Å, and N—H···Cl = 151 and 155°] between $[H_2bpz]^{2+}$ cations (square-planar node) and chloride anions (tetrahedral node), as complementary donors and acceptors of four hydrogen bonds, leads to a three-dimensional binodal four-connected framework with cooperite topology (three-letter notation pts). The framework contains channels along the c axis housing one-dimensional stacks of square-planar $[AuCl_4]^-$ anions [Au—Cl = 2.2895 (10)–2.2903 (16) Å; interanion Au···Cl contact = 3.489 (2) Å], which are excluded from primary hydrogen bonding with the $[H_2bpz]^{2+}$ tectons.

Comment

Strong N—H···X hydrogen bonding involving organic cations and halometallate species provides a range of characteristic motifs which can be used as supramolecular synthons for the developing field of ionic solids (Crawford *et al.*, 2004). In particular, cis-MCl$_2$···HN interactions, which dominate the structure of pyridinium salts containing $[PdCl_4]^{2-}$ and $[PtCl_4]^{2-}$ anions (Lewis & Orpen, 1998), have been widely explored for the construction of periodic chain-like structures based upon the alternation of halometallates and 4,4′-bipyridinium linkers (Adams *et al.*, 2006). However, the reliability of such halometallate–NH supramolecular synthons was insufficient in the case of less nucleophilic anions, such as tetrachloridoaurate(III). The hydrogen bonding in the prototypic (PyH)[AuCl$_4$] salt is very weak and does not even prevent

disorder of the pyridinium cations (Adams & Strähle, 1982), while systems based on the bifunctional 4,4′-bipyridinium (Zhang *et al.*, 2006) and 1,2-bis(pyridin-1-ium-4-yl)ethane and *trans*-1,2-bis(pyridin-1-ium-4-yl)ethene (Bourne & Moitsheki, 2008) tectons commonly exhibit crystallization of mixed anion chloride–tetrachloridoaurate(III) (1:1) species, in which the halometallates are excluded from bonding to the NH donors at all.

(I)
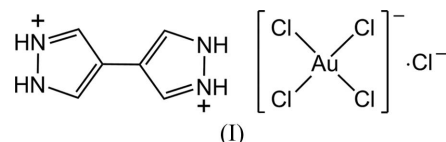
Therefore, a very illustrative example may be anticipated when considering doubling the NH donor functionality, as provided by symmetric 4,4′-bi(1H-pyrazol-2-ium) $[H_2bpz]^{2+}$ dications. Firstly, the multivalency of the pyrazolium donor and the proper and suitable orientation of the two adjacent NH donor sites may enhance the selectivity of the supramolecular interactions (Lukashuk *et al.*, 2011). This was best demonstrated with a special kind of supramolecular synthon employing double cis-MCl$_2$···pyrazolium bonding ($[PdCl_4]^{2-}$ and $[Cu_2Cl_6]^{2-}$; Boldog *et al.*, 2009), and it was interesting to question whether the less nucleophilic $[AuCl_4]^-$ could be used in a similar manner. Secondly, the combination of cationic multiple NH donors and Cl^- and $[AuCl_4]^-$ anions (which is typical within the pyridinium series) suggests the structural versatility of the system, concurrent N—H···Cl bonding, and new possiblities for designing hydrogen-bonded architectures by varying the NH-to-Cl^- ratio. In particular, the characteristic dimeric pyrazolium–chloride pattern (Boldog *et al.*, 2009) could presumably be expanded with the generation of the framework by the simple introduction of an additional $[H_2bpz]^{2+}$ 'spacer'. In this context, we have prepared the title new organic–inorganic hybrid salt, $[H_2bpz][AuCl_4]Cl$, (I).
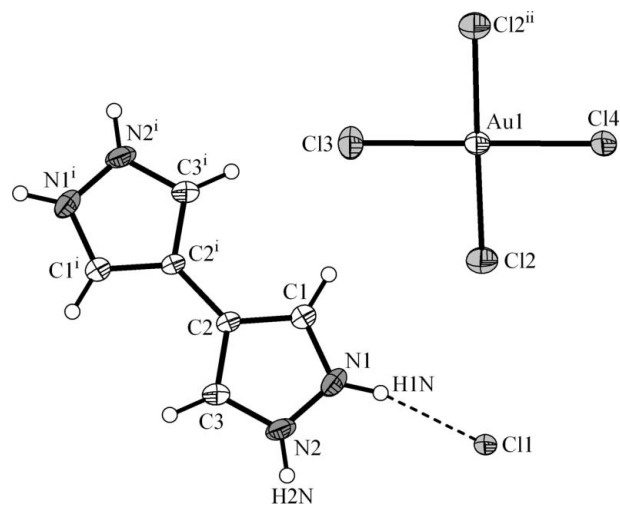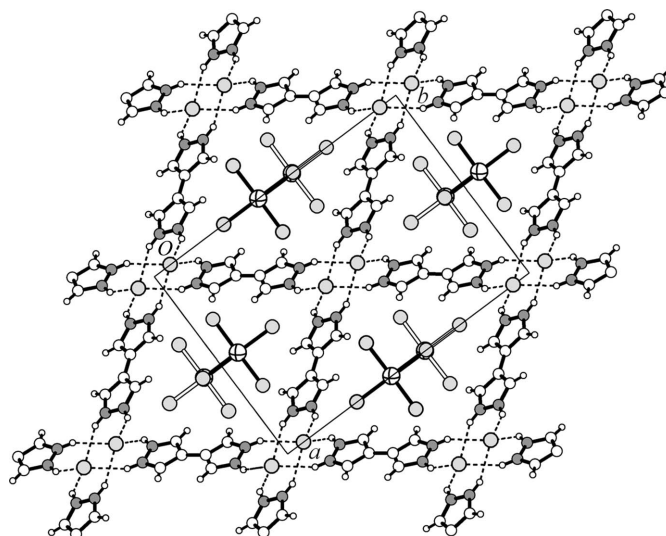

Figure 1
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. The dashed line indicates the N—H···Cl hydrogen bond. [Symmetry codes: (i) $-x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + 1$; (ii) $-x, y, -z + \frac{1}{2}$.]
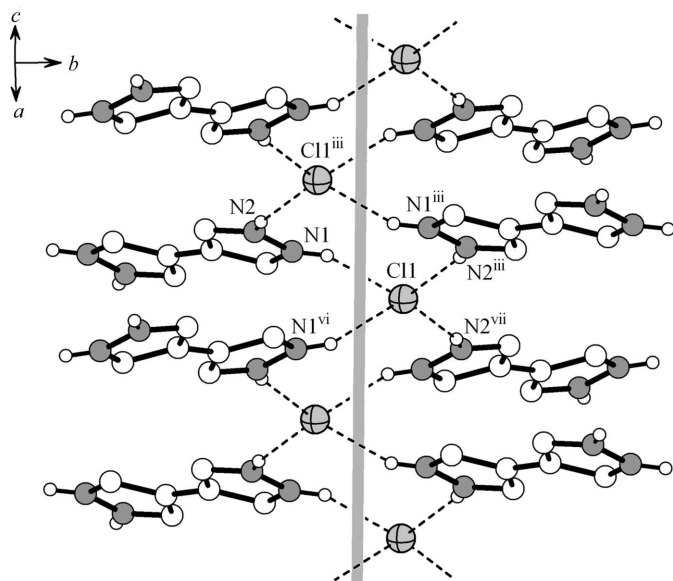
Figure 2
The pyrazolium–chloride hydrogen-bonding motif, leading to chains along the c direction. Note the centrosymmetric {Hpz$_2$Cl$_2$} cyclic patterns integrated within the present connectivity. C-bound H atoms have been omitted for clarity. [Symmetry codes: (iii) $-x + 1$, $-y + 1$, $-z + 2$; (vi) $-x + 1$, y, $-z + \frac{3}{2}$; (vii) x, $-y + 1$, $z - \frac{1}{2}$.]

Figure 3
A view of the three-dimensional hydrogen-bonded pts framework, down the c axis, showing how the tetrachloridoaurate(III) stacks are incorporated inside the channels. N atoms are shaded grey and dotted lines indicate hydrogen bonding.

In compound (I), the organic dication is situated across a centre of inversion, the chloride anion lies on a twofold rotation axis, and the [AuCl$_4$]$^-$ anion lies across a twofold rotation axis passing through atoms Cl3, Au1 and Cl4 (Fig. 1). The [AuCl$_4$]$^-$ anion has a standard square-planar geometry with four virtually identical Au—Cl distances (Table 1). The [H$_2$bpz]$^{2+}$ cation is planar to within ± 0.008 (3) Å. The equivalence of the N1H and N2H sites is indicated by uniform angles at the N atoms [C1—N1—N2 = 109.0 (3)° and C3—N2—N1 = 109.3 (3)°; Domasevitch, 2008], while in neutral 4,4′-bipyrazole these parameters are differentiated according to clearly distinguishable types: C—N—N(H) = 104.6 (2)° and C—N(H)—N = 112.0 (2)° (Boldog et al., 2001).

Inter-ion interactions occur by means of extensive N—H⋯Cl and C—H⋯Cl hydrogen bonding, while manifesting an appreciable discrimination of the halometallate hydrogen-bond acceptor in favour of the chloride anion. This agrees with the relatively poor hydrogen-bond acceptor ability of tetrachloridoaurate(III) (Calleja et al., 2001) and exactly parallels the behaviour of [AuCl$_4$]$^-$ towards 4,4′-bipyridinium and its extended analogues (Zhang et al., 2006; Bourne & Moitsheki, 2008). Therefore, the [AuCl$_4$]$^-$ anion is excluded from the primary bonding, which exists in the form of directional N—H⋯Cl1 interactions utilizing [H$_2$bpz]$^{2+}$ cations as fourfold donors and the chloride anions as complementary acceptors of four N—H⋯Cl bonds. These are actually uniform [N⋯Cl = 3.109 (3) and 3.127 (3) Å] (Table 2) and are typical for chloride salts of azole and azine bases. However, they are certainly weaker than those observed for the simple [H$_2$bpz]Cl$_2$ salt featuring discrete cyclic patterns {[Hpz]$_2$Cl$_2$} [N⋯Cl = 3.0308 (13) and 3.0444 (13) Å; Boldog et al., 2009]. This motif also remains intact for (I): the same cyclic patterns

are integrated into infinite polyspirane chains along the c axis by sharing Cl1 vertices (Fig. 2).

The bifunctional [H$_2$bpz]$^{2+}$ tectons extend this geometry in two other dimensions, giving rise to a three-dimensional cationic framework of composition {[H$_2$bpz]Cl}$_n^{n+}$, with channels of ca 5 × 5 Å running down the c direction (Fig. 3). Such evolution of the motif (one-dimensional {[H$_2$bpz]Cl$_2$}$_n$ to three-dimensional {[H$_2$bpz]Cl}$_n^{n+}$), while preserving the pyrazolium–chloride supramolecular synthon, occurs with a doubling of the [H$_2$bpz]$^{2+}$:Cl$^-$ ratio under a partial substitution of the Cl$^-$ acceptors for weakly nucleophilic [AuCl$_4$]$^-$ charge compensators. Considering the Cl1 anions as tetrahedral nodes and the organic dications as square-planar four-connected nodes, the entire topology of the hydrogen-bonded cationic framework is a binodal 4,4-coordinated net with a point Schläfli symbol {$4^2.8^4$} (topological type of cooperite; three-letter notation pts). Thus, the hydrogen-bond acceptor capacity of the chloride anion towards the pyrazolium cations is sufficient for the generation of four-connected nodes for the net, with a nearly tetrahedral geometry of the environment (H⋯Cl1⋯H = 78–123°), and the resulting framework clearly imprints the local geometry at two types of nodes. It is worth noting that the highest NH donor-to-Cl$^-$ ratio found for pyridinium cations does not exceed 3:1 {for example, in [PyH]$_3$[FeCl$_4$]$_2$Cl; Shaviv et al., 1992}, and therefore the pyrazolium and related five-membered azolium species could possess an even wider potential for the design of ionic crystals compared with pyridinium–chloride systems (Goldberg et al., 2006).

The channels in the structure of (I) provide sufficient space for the location of [AuCl$_4$]$^-$ anions, which form infinite stacks by long secondary interactions at both axial sites [Au1⋯Cl3^{viii} = 3.5815 (3) Å; symmetry code: (viii) $-x$, $-y + 1$, $-z + 1$] (Figs. 3 and 4), similar to what was observed for the 1-ethoxypropylimidium salt [Au⋯Cl = 3.489 (2) Å; Potts et

Figure 4
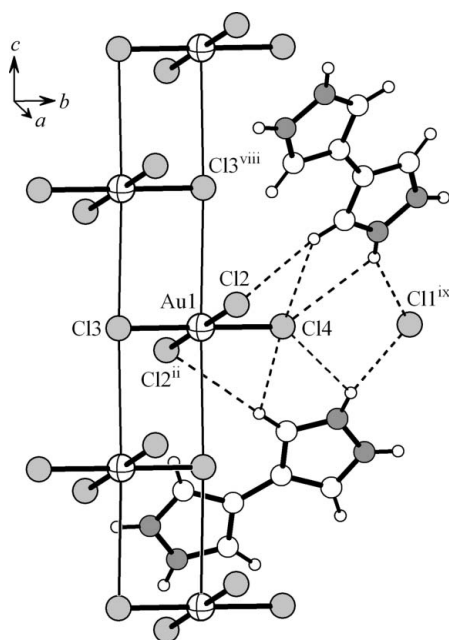The linear stack of [AuCl₄]⁻ anions involving secondary axial Au···Cl coordinations, and its weak hydrogen-bond interactions with [H₂bpz]²⁺ cations, constituting the framework. [Symmetry codes: (ii) $-x, y, -z + \frac{1}{2}$; (viii) $-x, -y + 1, -z + 1$; (ix) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.]

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.332 (5)	C2—C2ⁱ	1.459 (6)
N1—C1	1.338 (4)	Au1—Cl2	2.2895 (10)
N2—C3	1.331 (5)	Au1—Cl4	2.2903 (16)
C1—C2	1.379 (5)	Au1—Cl3	2.2903 (14)
C2—C3	1.387 (4)		
Cl2—Au1—Cl2ⁱⁱ	179.00 (5)	Cl2—Au1—Cl3	90.50 (3)
Cl2—Au1—Cl4	89.50 (3)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···Cl1	0.87	2.32	3.127 (3)	155
N2—H2N···Cl1ⁱⁱⁱ	0.87	2.32	3.109 (3)	151
N2—H2N···Cl4ⁱᵛ	0.87	2.93	3.449 (4)	120
C3—H3···Cl4ⁱᵛ	0.94	2.86	3.426 (3)	120
C3—H3···Cl2ᵛ	0.94	2.93	3.846 (4)	164

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

analysis calculated: C 14.12, H 1.58, N 10.98%; found: C 14.30, H 1.64, N 11.07%.

Crystal data

(C₆H₈N₄)[AuCl₄]Cl	$V = 1350.99$ (17) Å³
$M_r = 510.38$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 12.5768$ (8) Å	$\mu = 11.86$ mm⁻¹
$b = 16.0166$ (9) Å	$T = 213$ K
$c = 7.1617$ (5) Å	$0.11 \times 0.11 \times 0.09$ mm
$\beta = 110.533$ (10)°	

Data collection

Stoe IPDS diffractometer	6076 measured reflections
Absorption correction: numerical	1967 independent reflections
[*X-RED* (Stoe & Cie, 2001) and	1798 reflections with $I > 2\sigma(I)$
X-SHAPE (Stoe & Cie, 1999)]	$R_{int} = 0.025$
$T_{min} = 0.356$, $T_{max} = 0.415$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	76 parameters
$wR(F^2) = 0.060$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{max} = 1.69$ e Å⁻³
1967 reflections	$\Delta\rho_{min} = -1.31$ e Å⁻³

al., 1991]. Very weak hydrogen bonding between [AuCl₄]⁻ and [H₂bpz]²⁺ is indicated by a set of H···Cl contacts (Desiraju & Steiner, 1999) in the range 2.86–2.93 Å (Table 2). These may be attributed to a bifurcated C—H···Cl bond [shortest distance C3···Cl4ⁱᵛ = 3.426 (3) Å; symmetry code: (iv) $x + \frac{1}{2}$, $y - \frac{1}{2}, z + 1$] and the longer branch of a bifurcated N—H···Cl bond [N2···Cl4ⁱᵛ = 3.449 (4) Å] (Fig. 4); these are slightly shorter than in the [PyH][AuCl₄] salt [C(N)···Cl = 3.592 (3) Å; Adams & Strähle, 1982].

In summary, the framework structure and hydrogen-bonding patterns in (I) provide new insights into the design of ionic solids based upon cationic NH donors and halogenide and halometallate species. The multiple N—H···Cl⁻ hydrogen bonding of a potentially 'tetradentate' [H₂bpz]²⁺ tecton allows the assembly of a multidimensional hydrogen-bonded framework, similar to the contruction of coordination polymers, while exploiting *N*-coordination to the metal ions. Variations in the [H₂bpz]²⁺-to-acceptor ratio, feasible with the incorporation of additional low-nucleophilic anions ([AuCl₄]⁻ versus Cl⁻ hydrogen-bond acceptors), allow control over the dimensionality of the framework.

Experimental

4,4′-Bipyrazole (bpz) was prepared by a multistage synthesis starting from butyne-1,4-diol (Boldog *et al.*, 2001). For the preparation of (I), solutions of bpz (0.0268 g, 0.2 mmol) in 20% HCl (4 ml) and HAuCl₄ [prepared from 0.078 g (0.4 mmol) of gold metal] in 20% HCl (2 ml) were mixed, filtered and allowed to evaporate at room temperature for a period of 20–30 d. Small orange prisms of the product, (I) (yield 0.061 g; 60%, based on the organic component), were filtered off, washed with a few drops of 10% HCl and dried in air. Elemental

All H atoms were located from difference maps and were then refined as riding with the angles constrained; N—H = 0.87 Å and C—H = 0.94 Å, with $U_{iso}(H) = 1.5U_{eq}(N)$ or $1.2U_{eq}(C)$.

Data collection: *IPDS Software* (Stoe & Cie, 2000); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

metal-organic compounds

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