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Piperazine-1,4-dium bis[tetrachloridoaurate(III)] dihydrate

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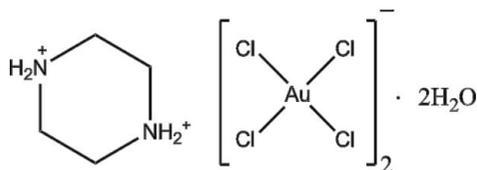
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 Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.018; wR factor = 0.044; data-to-parameter ratio = 29.6.

In the title compound, $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{AuCl}_4]_2 \cdot 2\text{H}_2\text{O}$, the Au^{III} atom has a square-planar geometry. The piperazinium dication lies on an inversion centre and adopts a typical chair conformation. In the crystal, a combination of $\text{N}-\text{H} \cdots \text{O}$, $\text{N}-\text{H} \cdots \text{Cl}$ and $\text{O}-\text{H} \cdots \text{Cl}$ hydrogen bonds results in the formation of a three-dimensional network.

Related literature

For bond distances, see: Allen *et al.* (1987). For similar compounds, see: Kefi & Nasr (2005); Sharutin *et al.* (2008); Sutherland & Harrison (2009); Zhang *et al.* (2006).



Experimental

Crystal data

 $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{AuCl}_4]_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 801.72$

 Monoclinic, $P2_1/c$
 $a = 7.7327$ (11) Å

 $b = 10.1114$ (15) Å

 $c = 11.9024$ (18) Å

 $\beta = 105.565$ (3)°

 $V = 896.5$ (2) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 17.53$ mm⁻¹
 $T = 296$ K

 $0.33 \times 0.23 \times 0.08$ mm

Data collection

Bruker SMART CCD 1000 diffractometer

 Absorption correction: gaussian (*XPREP* and *SADABS*; Bruker, 2003)

 $T_{\text{min}} = 0.043$, $T_{\text{max}} = 0.251$

6689 measured reflections

2630 independent reflections

 2446 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.044$
 $S = 1.09$

2630 reflections

89 parameters

2 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 1.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.75$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1B} \cdots \text{O1}^{\text{i}}$	0.90	1.97	2.815 (3)	155
$\text{N1}-\text{H1B} \cdots \text{O1}^{\text{ii}}$	0.90	2.39	2.960 (3)	121
$\text{O1}-\text{H2} \cdots \text{Cl1}^{\text{iii}}$	0.839 (13)	2.57 (2)	3.3035 (19)	147 (3)
$\text{O1}-\text{H2} \cdots \text{Cl4}^{\text{iii}}$	0.839 (13)	2.83 (3)	3.445 (2)	131 (3)
$\text{O1}-\text{H1} \cdots \text{Cl4}$	0.822 (14)	2.71 (3)	3.382 (2)	140 (3)
$\text{O1}-\text{H1} \cdots \text{Cl3}$	0.822 (14)	2.67 (3)	3.268 (2)	131 (3)
$\text{N1}-\text{H1A} \cdots \text{Cl1}$	0.90	2.60	3.373 (2)	144
$\text{N1}-\text{H1A} \cdots \text{Cl2}$	0.90	2.81	3.575 (2)	143

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2149).

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supporting information

Acta Cryst. (2009). E65, m1377 [https://doi.org/10.1107/S1600536809041063]

Piperazine-1,4-dium bis[tetrachloridoaurate(III)] dihydrate

Anna V. Polishchuk, Emilia T. Karaseva and Mikhail A. Pushilin

S1. Comment

The asymmetric unit of the title compound consists of a discrete $[\text{AuCl}_4]^-$ complex anion, one water molecule and one-half of a diprotonated piperazinium dication (Fig. 1). The Au atom in the tetrachloridoaurate anion exhibits a square-planar coordination. A similar geometry has been observed, for example, in tetraphenylantimony(V) tetrachloroaurate (Sharutin *et al.*, 2008) and bipyridinium tetrachloroaurate (Zhang *et al.*, 2006). The Au—Cl bond lengths are in the range of 2.2802 (6) - 2.2842 (7) Å. In the crystal structure, the anions are stacked into columns along the *a* axis, parallel to each other. The distances between anion planes are ca. 3.734 and 3.999 Å. The organic piperazinium dication lies at an inversion centre and adopts a typical chair geometry with normal valence bond lengths (Allen *et al.*, 1987) and angles, as observed in the structures of piperazinediium tetrachloridozincate (Sutherland & Harrison, 2009) and piperazinediium tetrachloridozincate monohydrate (Kefi & Nasr, 2005).

The piperazinium dications and water molecules are linked by intermolecular bifurcated N—H \cdots O hydrogen bonds to form chains proagagting along the [100] direction (Fig. 2). The water-piperazinium chains and the anion stacks form a three-dimensional framework (Fig. 3) via bifurcated N—H \cdots Cl and O—H \cdots Cl hydrogen bonds (Table 1).

S2. Experimental

The chemicals used were of reagent grade. Ciprofloxacin hydrochloride (37 mg, 0.1 mmol) and gold(III) chloride (AuCl_3 , 30 mg, 0.1 mmol) were dissolved in 10 ml of 32% of HCl. Yellow crystals of the title compound, suitable for X-ray analysis, were obtained by slow evaporation in air at rt, after a few days.

S3. Refinement

The water H-atoms were located from difference electron-density maps and were refined with distance restraints of O—H = 0.85 (2) Å and $U_{iso}(\text{H}) = 1.5U_{eq}(\text{O})$. All the other H-atoms were positioned geometrically and allowed to ride on their parent atoms: N—H = 0.90 Å, C—H = 0.97 Å with $U_{iso}(\text{H}) = 1.2U_{eq}(\text{parent N or C atom})$.

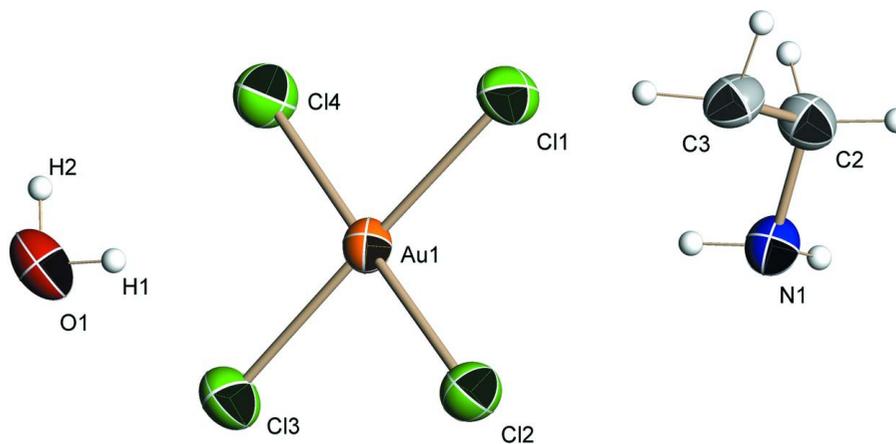


Figure 1

The asymmetric unit of the title compound, showing 50% displacement ellipsoids (arbitrary spheres for the H atoms).

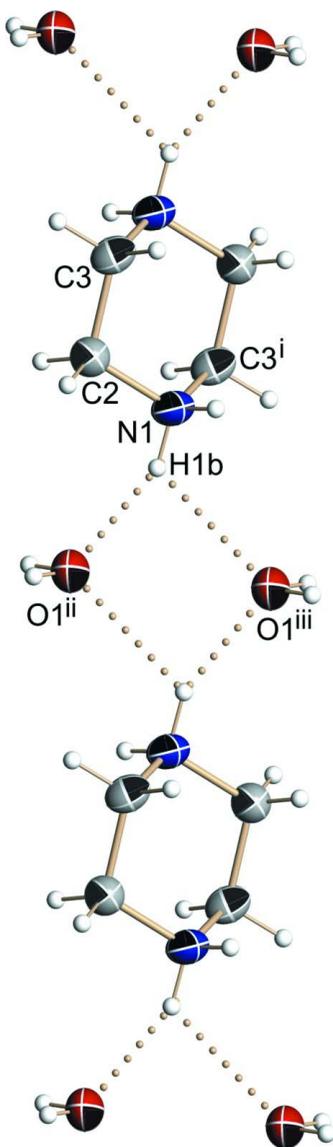


Figure 2

Fragment of the water-piperazinium hydrogen bonded chain, with the hydrogen bonds indicated by dotted lines. Symmetry codes are the same as in Table 1.

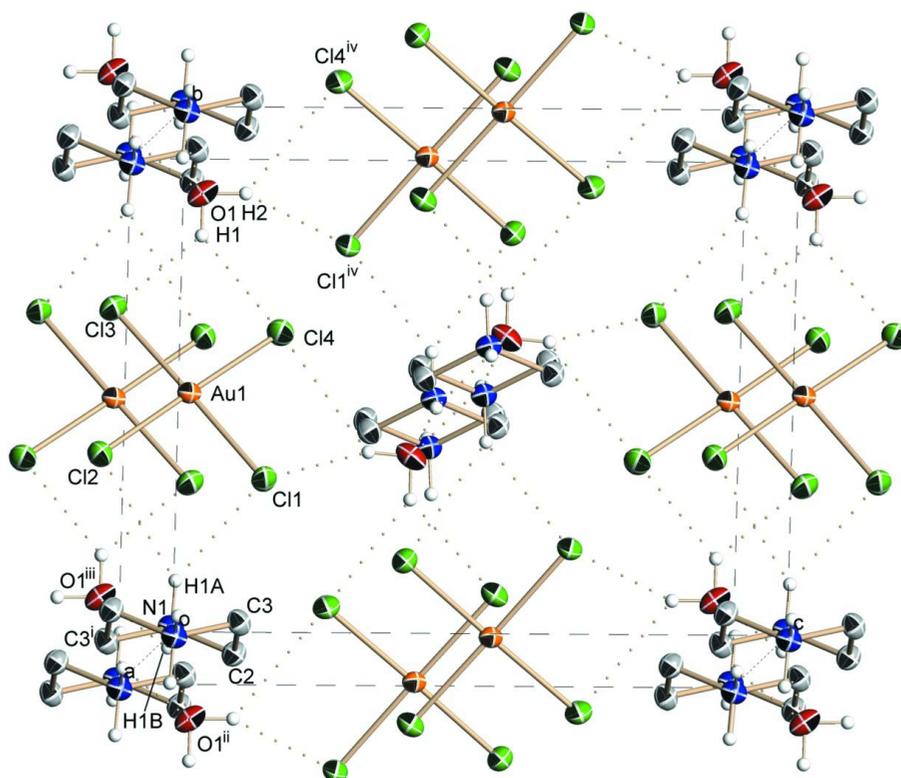


Figure 3

A view along the *a* axis of the crystal packing of the title compound, with the hydrogen bonds shown as dotted lines. All the C-bound H atoms have been omitted for clarity. Symmetry codes are the same as in Table 1.

Piperazine-1,4-dium bis[tetrachloridoaurate(III)] dihydrate

Crystal data

(C₄H₁₂N₂)[AuCl₄]₂·2H₂O

M_r = 801.72

Monoclinic, *P*2₁/*c*

Hall symbol: -*P* 2ybc

a = 7.7327 (11) Å

b = 10.1114 (15) Å

c = 11.9024 (18) Å

β = 105.565 (3)°

V = 896.5 (2) Å³

Z = 2

F(000) = 728

D_x = 2.970 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 1008 reflections

θ = 3.4–30.6°

μ = 17.53 mm⁻¹

T = 296 K

Prism, yellow

0.33 × 0.23 × 0.08 mm

Data collection

Bruker SMART CCD 1000
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.33 pixels mm⁻¹

ω scans

Absorption correction: gaussian

(*XPRED* and *SADABS*; Bruker, 2003)

T_{min} = 0.043, *T_{max}* = 0.251

6689 measured reflections

2630 independent reflections

2446 reflections with *I* > 2σ(*I*)

R_{int} = 0.018

θ_{max} = 31.5°, θ_{min} = 2.7°

h = -10→9

k = -13→12

l = -14→17

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.044$
 $S = 1.09$
 2630 reflections
 89 parameters
 2 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 0.7643P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.36 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.75 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.01512 (17)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.258077 (10)	0.481141 (8)	0.040268 (7)	0.03248 (2)
Cl1	0.22668 (9)	0.31457 (6)	0.16243 (5)	0.04886 (14)
Cl2	0.12348 (9)	0.34990 (6)	-0.11438 (5)	0.04885 (15)
Cl3	0.29217 (10)	0.64504 (6)	-0.08394 (6)	0.05264 (16)
Cl4	0.39054 (10)	0.60981 (7)	0.19756 (6)	0.05297 (16)
O1	0.5108 (2)	0.88550 (19)	0.07637 (17)	0.0495 (4)
H1	0.499 (5)	0.8047 (14)	0.075 (3)	0.074*
H2	0.546 (5)	0.890 (4)	0.1494 (12)	0.074*
N1	0.1859 (2)	0.02747 (18)	0.01336 (18)	0.0360 (4)
H1A	0.1882	0.1163	0.0188	0.043*
H1B	0.2985	-0.0004	0.0190	0.043*
C2	0.1246 (3)	-0.0285 (2)	0.1115 (2)	0.0390 (5)
H2A	0.2018	0.0029	0.1849	0.047*
H2B	0.1330	-0.1242	0.1106	0.047*
C3	-0.0679 (3)	0.0117 (2)	0.1018 (2)	0.0384 (5)
H3A	-0.1087	-0.0305	0.1632	0.046*
H3B	-0.0741	0.1067	0.1113	0.046*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.03239 (3)	0.02880 (4)	0.03751 (4)	0.00020 (3)	0.01157 (3)	-0.00039 (3)
Cl1	0.0685 (3)	0.0368 (3)	0.0414 (3)	-0.0146 (2)	0.0150 (2)	0.0013 (2)

C12	0.0623 (3)	0.0419 (3)	0.0398 (3)	-0.0061 (3)	0.0092 (2)	-0.0053 (2)
C13	0.0701 (4)	0.0397 (3)	0.0488 (3)	-0.0048 (3)	0.0172 (3)	0.0087 (2)
C14	0.0677 (3)	0.0412 (3)	0.0463 (3)	-0.0155 (3)	0.0088 (3)	-0.0056 (2)
O1	0.0402 (7)	0.0474 (9)	0.0594 (10)	0.0011 (7)	0.0107 (7)	0.0196 (8)
N1	0.0297 (7)	0.0361 (9)	0.0450 (9)	-0.0024 (6)	0.0151 (7)	-0.0022 (7)
C2	0.0357 (9)	0.0425 (12)	0.0386 (11)	0.0013 (8)	0.0096 (8)	0.0047 (8)
C3	0.0371 (9)	0.0442 (11)	0.0382 (10)	-0.0045 (8)	0.0176 (8)	-0.0048 (8)

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

Au1—C11	2.2802 (6)	N1—H1A	0.9000
Au1—C12	2.2813 (6)	N1—H1B	0.9000
Au1—C13	2.2827 (7)	C2—C3	1.517 (3)
Au1—C14	2.2842 (7)	C2—H2A	0.9700
O1—H1	0.822 (14)	C2—H2B	0.9700
O1—H2	0.839 (13)	C3—H3A	0.9700
N1—C3 ⁱ	1.482 (3)	C3—H3B	0.9700
N1—C2	1.486 (3)		
C11—Au1—C12	88.92 (3)	N1—C2—C3	110.55 (18)
C11—Au1—C13	178.87 (3)	N1—C2—H2A	109.5
C12—Au1—C13	90.39 (3)	C3—C2—H2A	109.5
C11—Au1—C14	89.95 (3)	N1—C2—H2B	109.5
C12—Au1—C14	178.82 (2)	C3—C2—H2B	109.5
C13—Au1—C14	90.74 (3)	H2A—C2—H2B	108.1
H1—O1—H2	94 (3)	N1 ⁱ —C3—C2	110.31 (19)
C3 ⁱ —N1—C2	112.20 (17)	N1 ⁱ —C3—H3A	109.6
C3 ⁱ —N1—H1A	109.2	C2—C3—H3A	109.6
C2—N1—H1A	109.2	N1 ⁱ —C3—H3B	109.6
C3 ⁱ —N1—H1B	109.2	C2—C3—H3B	109.6
C2—N1—H1B	109.2	H3A—C3—H3B	108.1
H1A—N1—H1B	107.9		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1B \cdots O1 ⁱⁱ	0.90	1.97	2.815 (3)	155
N1—H1B \cdots O1 ⁱⁱⁱ	0.90	2.39	2.960 (3)	121
O1—H2 \cdots C11 ^{iv}	0.84 (1)	2.57 (2)	3.3035 (19)	147 (3)
O1—H2 \cdots C14 ^{iv}	0.84 (1)	2.83 (3)	3.445 (2)	131 (3)
O1—H1 \cdots C14	0.82 (1)	2.71 (3)	3.382 (2)	140 (3)
O1—H1 \cdots C13	0.82 (1)	2.67 (3)	3.268 (2)	131 (3)
N1—H1A \cdots C11	0.90	2.60	3.373 (2)	144
N1—H1A \cdots C12	0.90	2.81	3.575 (2)	143

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