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p-Phenylenediammonium tetrabromoaurate(III) bromide monohydrate

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Key indicators

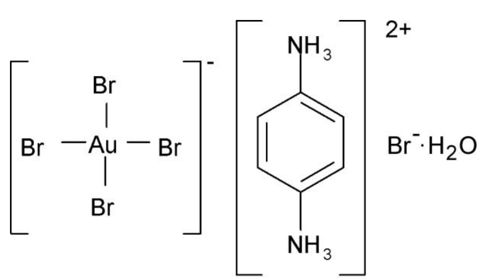
Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.020 Å
R factor = 0.082
wR factor = 0.211
Data-to-parameter ratio = 22.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title compound, $(C_6H_{10}N_2)[AuBr_4]Br\cdot H_2O$, consists of twin parallel stacks of square-planar $[AuBr_4^-]$ polyhedra ordered along the *a* axis. The stacks are interleaved such that one Br atom of the $AuBr_4^-$ square planes of one twin stack lies directly above or behind the Au atom from the neighboring stack, creating a pseudo-Jahn–Teller-like distorted octahedral coordination environment around the Au^{III} ions. The twin stacks are separated by parallel stacks of *p*-phenylenediammonium cations, and the structure is presumably held together by coulombic forces between the interdigitated negatively and positively charged one-dimensional stacks. The water molecule, the tetrabromoaurate anion and the bromide anion all lie on mirror planes.

Comment

Gold halides, and other gold compounds, have long been used in the sensitization of photographic silver halide emulsions (Harbison & Spencer, 1977; Mueller, 1966; Tani & Toshida, 2000; Charlier *et al.*, 2000). Gold 'dopants' may act as electron traps, and improve the efficiency of latent image formation and the sensitivity of photographic emulsions. We report here the synthesis and crystal structure (Fig. 1) determination of $(C_6H_{10}N_2)[AuBr_4]Br\cdot H_2O$, (I), a unique, self-assembled complex of gold bromide and the color photographic developer 1,4-benzenediamine [often referred to as *para*-phenylenediamine (PPD)]. Earlier, we reported the synthesis and crystal structure of closely related compounds, $Ag_2Br_6(PPD)_2$, $Ag_2I_6(CD\text{-}2)_2\cdot H_2O$, $Ag_2Br_6(CD\text{-}2)_2\cdot H_2O$, $Ag_2Br_6(TMBD)_2$ (Bringley *et al.*, 2005) and $ZnCl_4(PPD)$ (Bringley & Rajeswaran, 2006) (where CD-2 is *N*,*N*-diethyl-2-methyl-1,4-benzenediamine and TMBD is *N*,*N*,*N*′,*N*′-tetramethyl-1,4-benzenediamine).



(I)

The synthetic methodology for preparing the title compound is adapted from the methodology used to prepare silver halide/developer complexes (Bringley *et al.*, 2005). We show here that this methodology can be used to prepare unique structures in which a gold halide is complexed with protonated color-developer molecules. The protonation of the

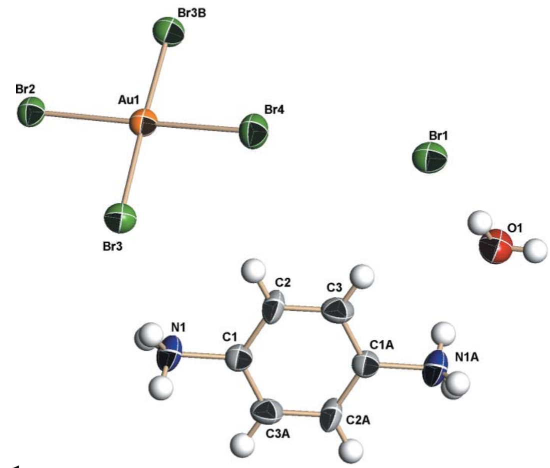


Figure 1
View of (I), showing the atomic numbering scheme. Symmetry codes: (A) $-x, -y, -z$; (B) $x, \frac{1}{2} - y, z$. Displacement ellipsoids are drawn with 50% probability.

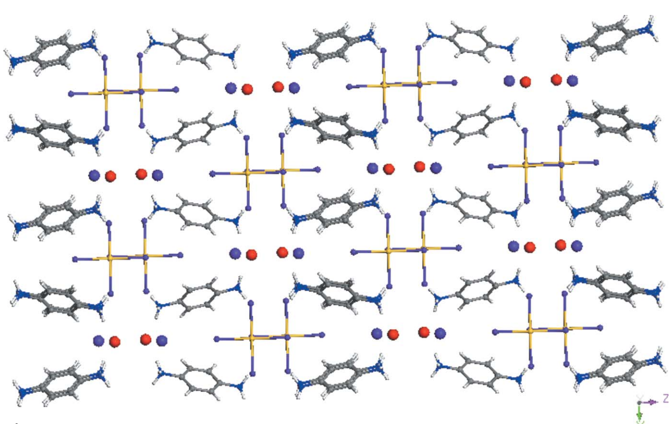


Figure 2
Packing in the structure of (I), illustrating twin parallel stacks of square planar $[AuBr_4^-]$ polyhedra ordered along the *a* axis.

developer shuts down its ability to reduce gold ions, and thus stabilizes the compound against reduction to gold metal. Upon a pH switch, as in development, the compound can be shown to rapidly convert back to the starting materials, yielding $[AuX_4]^-$ and an active developer:

AuX_4(organoammonium) → $[AuX_4]^-$ + organoamine.

Complexes of this nature, and those discussed elsewhere (Bringley *et al.*, 2005; Bringley & Liebert, 2003), might potentially be used as unique photographic addenda that might be capable of simultaneously delivering gold(III) ions and color developer directly to the developing grains. The availability of these species, dispersed on an atomic or molecular scale, would be expected to have a profound influence on the development processes, especially in the early stages of development.

Au1, Br2, Br4 and Br1 lie on a mirror plane; the cation lies on a center of inversion. Selected geometric parameters for Au1 are listed in Table 1. The Au ion in the tetrabromo anion shows the common square-planar coordination, a geometry which is common for such tetrahalo anions (Adams & Strähle, 1982; Zhang *et al.*, 2006). The structure of $(C_6H_{10}N_2)[AuBr_4]$-$Br\cdot H_2O$ consists of twin parallel stacks of square-planar $[AuBr_4^-]$ polyhedra ordered along the *a* axis (Fig. 2). The stacks are interleaved such that one Br atom of the $[AuBr_4^-]$ square plane of one twin stack lies directly above or behind the Au atom from the neighboring stack. This creates a pseudo-Jahn–Teller-like distorted octahedral coordination environment around the gold(III) ions in the structure. The twin stacks are separated by parallel stacks of *para*-phenylenediammonium cations, and the structure is presumably held together by coulombic forces between the inter-digitated negatively and positively charged one-dimensional stacks. The structure is likely also held together by an extensive network of hydrogen-bonding forces (Table 2) present between the stacks.

Experimental

The title compound was synthesized by dissolving 1,4-phenylenediamine·2HCl (Aldrich) (0.120 g, 0.65 mmol) in a mixture of 15 ml of 48% aqueous HBr and 10 ml of distilled water and heating to about 313 K. Separately, $K[AuCl_4]$ (0.5 g, 1.323 mmol) was dissolved in 5 ml of 48% aqueous HBr and 2.5 ml distilled water and the solution was heated to 313 K. The two solutions were then combined, held at 323 K for about 1 h, and allowed to cool to room temperature. The reaction mixture was placed in a refrigerator at 277 K for two days. Ruby-red needle-like crystals were collected by vacuum filtration and dried under flowing nitrogen. (Yield 0.41 g, 85%.) Elemental analysis (calculated) found: C (9.94) 9.93, H (1.67) 1.75, N (3.86) 3.88%.

Crystal data

$(C_6H_{10}N_2)[AuBr_4]Br\cdot H_2O$
$M_r = 724.69$
Orthorhombic, *Pnma*
$a = 6.8462$ (3) Å
$b = 11.4379$ (7) Å
$c = 19.2654$ (7) Å
$V = 1508.60$ (13) Å^3
$Z = 4$
$D_x = 3.191$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 22.97$ mm^{-1}
$T = 293$ (2) K
Needle, red
0.22 × 0.05 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.113$, $T_{max} = 0.434$ (expected range = 0.083–0.317)
7709 measured reflections
1739 independent reflections
1062 reflections with $I > 2\sigma(I)$
$R_{int} = 0.100$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.082$
$wR(F^2) = 0.211$
$S = 1.00$
1739 reflections
76 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1306P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 7.13$ e Å^{-3}
$\Delta\rho_{min} = -4.83$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Au1—Br4	2.427 (2)	Au1—Br2	2.454 (2)
Au1—Br3	2.434 (2)		
Br4—Au1—Br3	89.74 (4)	Br4—Au1—Br2	178.24 (8)
Br4—Au1—Br3^i	89.74 (4)	Br3—Au1—Br2	90.32 (4)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1S···Br1	0.87	2.40	3.262 (16)	176.7
O1—H2S···Br1^{ii}	0.86	2.43	3.285 (15)	172.2
N1—H1A···O1^{iii}	0.87	2.23	2.887 (17)	132.9
N1—H1A···Br1^{iv}	0.87	2.81	3.311 (13)	118.4
N1—H1B···Br1^{iv}	0.88	2.70	3.311 (13)	127.9
N1—H1B···Br3	0.88	2.92	3.703 (12)	149.2
N1—H1C···Br3^{v}	0.86	2.77	3.487 (12)	142.1
N1—H1C···Br2^{v}	0.86	2.93	3.515 (15)	127.6

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

The quality of the crystals was not very good as indicated by a rather high $R_{\rm int}$ value, but we were unable to produce better quality single crystals. The positions of all of the H atoms were generated geometrically (C—H = 0.93 Å, N—H and O—H as in Table 2), assigned isotropic displacement parameters [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N,O)], and allowed to ride on their respective parent C atoms. In the final difference Fourier map, the highest residual electron density is 1.05 Å from Au1 and the deepest hole is 0.87 Å from Au1.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXTL* (Bruker, 2000); molecular graphics: *SHELXTL* (Bruker, 2000) and *MaterialsStudio* (Accelrys, 2002); software used to prepare material for publication: *SHELXTL*.

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