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catena-Poly[tetramethylammonium [argentate(I)-di-μ-bromido]]

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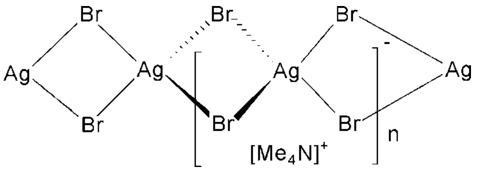
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–N) = 0.005 Å; some non-H atoms missing; R factor = 0.030; wR factor = 0.068; data-to-parameter ratio = 16.5.

The title compound, $\{(C_4H_{12}N)[AgBr_2]\}_n$, is isomorphous with its chloride analogue [Helgesson, Josefsson & Jagner (1988). *Acta Cryst.* C**44**, 1729–1731]. It displays a one-dimensional $^{\infty}_{1}[Ag_2Br_4]_n^{2n-}$ anionic chain structure accompanied by isolated tetramethylammonium cations. All the crystallographically independent non-H atoms lie on special positions, namely Ag on $2mm$, Br on $mm2$ or $m2m$, N on $mm2$, and C on sites of symmetry m_a or m_b. The tetramethylammonium cations reside between these anionic chains, with weak C—H⋯Br hydrogen-bonding interactions forming a layer perpendicular to the c axis; these layers stack together along the c direction merely by van der Waals forces.

Related literature

For related literature, see: Bringley *et al.* (2005), and references therein; Helgesson *et al.* (1988); Helgesson & Jagner (1991); Liu *et al.* (2005, 2006); Steiner (1996); Stomberg (1969).



Experimental

Crystal data

$(C_4H_{12}N)[AgBr_2]$
M_r = 341.84
Orthorhombic, $Immm$
a = 6.7817 (9) Å
b = 9.1535 (14) Å
c = 15.057 (2) Å
V = 934.7 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 10.63 mm^{-1}
T = 293 (2) K
0.20 × 0.20 × 0.16 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (*SPHERE* in *CrystalClear*; Rigaku, 2002)
$T_{\min}$ = 0.13, $T_{\max}$ = 0.18
2952 measured reflections
494 independent reflections
459 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.068
S = 1.00
494 reflections
30 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.65 e Å^{-3}
$\Delta\rho_{\min}$ = −0.77 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ag1—Br2	2.7006 (5)	Ag1—Br1	2.7221 (5)
Br2$^{\rm i}$—Ag1—Br2	107.14 (2)	Br1—Ag1—Br1$^{\rm ii}$	97.93 (2)
Br2—Ag1—Br1	112.947 (7)		

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C2—H2C⋯Br1$^{\rm iii}$	0.96	2.85	3.802 (4)	172

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

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *ORTEP* (Johnson, 1976); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG3057).

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supplementary materials

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catena-Poly[tetramethylammonium [argentate(I)-di-μ-bromido]]

X. Liu

Comment

Great interest is presently being focused on the controllable preparation of silver-halide-organoamonium compounds due to their potential application in photographic, photothermal, and other imaging or printing modalities (Bringley *et al.*, 2005, and references therein). In these photographic functional compounds, the $[Ag_aX_b]^{n-}$ parts may serve as commercial photographic color developer molecules. The reactions of silver(I) cyanide with Me_4NBr (tetramethylammonioum) in acetonitrile solution and then diffused with aether lead to a AgBr-based complex, $[Me_4N]_2[Ag_2Br_4]$ (I), isomorphous to its Cl analogue, reported by Helgesson *et al.*, 1988.

Compound (I) displays a one-dimensional ${}^{\infty}{}_1[Ag_2Br_4]_n{}^{2n-}$ anionic chain structure accompanied with isolated $[Me_4N]^+$ cations. As shown in Figure 1, one crystallographically independent silver cation in the center of a slightly distorted tetrahedral geometry is coordinated by four µ-Br atoms. The Ag—Br bond distances range from 2.7006 (5) to 2.7221 (5) Å, and the Br—Ag—Br bond angels vary between 97.93 (2) to 112.947 (7) °, in agreement with those in the $[Ag_aBr_b]^{n-}$ clusters (Stomberg, 1969; Helgesson & Jagner, 1991; Liu *et al.*, 2006). The silver cations are double bridged by µ-Br atoms to form an one-dimensional ${}^{\infty}{}_1[Ag_2Br_4]_n{}^{2n-}$ anionic chain along the *a* direction, which also can be regarded as the common chain formed by edge-sharing $[AgBr_4]^{3-}$ tetrahedrons (Stomberg, 1969; Helgesson & Jagner, 1991). While the $[Me_4N]^+$ cations reside between these anionic chains with weak C—H···Br hydrogen bonding interactions (Steiner, 1996; Liu *et al.*, 2005) to form a special layer along the *a* and *b* directions (Figure 2). These special layers further stack together along the *c* direction merely by *Van der Waals* forces.

Solid-state luminescence spectra show that comound I exhibits a broad strong blue emission band centered around 485 nm upon photo-excitation at 300 nm (Figure 3) and its lifetime was measured to be 3.3 µs, suggesting to be a potential candidate for luminescent material. Density of states (DOS) calculation sindicate that the top of valence bands (VBs) are mostly formed by Ag-4 d state mixing with Br-4p state, while the bottom of conduction bands (CBs) are almost contribution from the Br-4 s state, indicating the luminescent emission probably originated from metal-to-ligand charge transfer (MLCT) accompanied with hybridizations between Ag-4 d and Br-4p.

Experimental

A mixture of AgCN (238 mg, 1.8 mmol) and Me_4NBr (139 mg, 0.9 mmol) in 10 ml of dry and distilled acetonitrile was sealed into a 25 ml polytetrafluoroethylene-lined stainless steel containers under autogenous pressure and heated at 120 °C for 3 days, followed by cooling to room temperature. The resulted solution was filtered in a small tube, which was loaded into a large vial containing 5 ml diethyl ether. The large vial was sealed and left undisturbed at room temperature, and colourless crystals of the title complex were obtained in 7 days. Yield: 40%. Calc. for $C_8H_{24}Ag_2Br_4N_2$: C, 14.05; H, 3.54; N, 4.10; Found: C, 14.12; H, 3.60; N, 4.02.

Refinement

Methyl H atoms were added geometrically and allowed to ride on their respective parent carbon atoms (C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$). The groups were also allowed to rotate around the N—C vector.

Figures

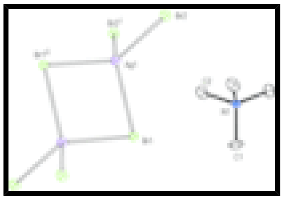

Fig. 1. *ORTEPII* (Johnson, 1976) plot of I at 30% probability of thermal ellipsoids. All hydrogen atoms are omitted for clarity. Symmetry codes i: −1 − *x*, −*y*, 1 − *z*; ii: −2 − *x*, −*y*, 1 − *z*

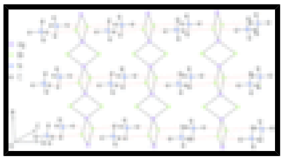

Fig. 2. A view of the weak C—H···Br hydrogen bonding interactions between the $^{\infty}{}_{1}[Ag_2Br_4]_n{}^{2n-}$ anionic chains and $[Me_4N]^+$ cations, which are represented as dashed lines.

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Crystal data

$(C_4H_{12}N)[AgBr_2]$

$M_r = 341.84$

Orthorhombic, *Immm*

Hall symbol: -I 2 2

$a = 6.7817\ (9)$ Å

$b = 9.1535\ (14)$ Å

$c = 15.057\ (2)$ Å

$V = 934.7\ (2)$ Å^3

$Z = 4$

$F_{000} = 640$

$D_x = 2.429$ Mg m^{-3}

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

Cell parameters from 972 reflections

$\theta = 3.3–27.5°$

$\mu = 10.63$ mm^{-1}

$T = 293\ (2)$ K

Prism, colourless

0.20 × 0.20 × 0.16 mm

Data collection

Rigaku Mercury CCD
diffractometer

Radiation source: rotating-anode generator

Monochromator: graphite

$T = 293(2)$ K

ω scans

Absorption correction: multi-scan
(SPHERE in CrystalClear; Rigaku, 2002)

$T_{min} = 0.13$, $T_{max} = 0.18$

2952 measured reflections

494 independent reflections

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

$R_{int} = 0.031$

$\theta_{max} = 25.0°$

$\theta_{min} = 3.3°$

$h = -8\rightarrow8$

$k = -10\rightarrow10$

$l = -9\rightarrow17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.030$	$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 4.8P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.00$	$\Delta\rho_{max} = 0.65$ e Å^{-3}
494 reflections	$\Delta\rho_{min} = -0.77$ e Å^{-3}
30 parameters	Extinction correction: SHELXTL (Siemens, 1994), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.00064 (14)
Secondary atom site location: difference Fourier map	

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Ag1	0.26353 (6)	0.5000	0.5000	0.05861 (12)	
Br1	0.0000	0.5000	0.36364 (3)	0.05356 (14)	
Br2	0.5000	0.26262 (5)	0.5000	0.05680 (15)	
N1	0.5000	0.5000	0.1917 (3)	0.0490 (11)	
C1	0.3206 (6)	0.5000	0.1370 (3)	0.121 (2)	
H1A	0.3205	0.4156	0.0992	0.181*	0.50
H1B	0.3174	0.5868	0.1013	0.181*	0.50
H1C	0.2067	0.4976	0.1748	0.181*	
C2	0.5000	0.6304 (4)	0.2516 (3)	0.0781 (14)	
H2A	0.6152	0.6282	0.2887	0.117*	0.50
H2B	0.3840	0.6288	0.2882	0.117*	0.50
H2C	0.5008	0.7179	0.2165	0.117*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

Ag1	0.0521 (2)	0.0711 (2)	0.0526 (2)	0.000	0.000	0.000
Br1	0.0402 (2)	0.0777 (3)	0.0428 (2)	0.000	0.000	0.000
Br2	0.0566 (3)	0.0474 (3)	0.0664 (3)	0.000	0.000	0.000
N1	0.0416 (19)	0.061 (2)	0.044 (2)	0.000	0.000	0.000
C1	0.064 (3)	0.224 (7)	0.073 (3)	0.000	−0.035 (2)	0.000
C2	0.072 (2)	0.051 (2)	0.111 (3)	0.000	0.000	−0.005 (2)

Geometric parameters (Å, °)

Ag1—Br2^{i}	2.7006 (5)	N1—C2^{iii}	1.496 (5)
Ag1—Br2	2.7006 (5)	C1—H1A	0.9600
Ag1—Br1	2.7221 (5)	C1—H1B	0.9600
Ag1—Br1^{ii}	2.7221 (5)	C1—H1C	0.9600
N1—C1	1.470 (5)	C2—H2A	0.9600
N1—C1^{iii}	1.470 (5)	C2—H2B	0.9600
N1—C2	1.496 (5)	C2—H2C	0.9600
Br2^{i}—Ag1—Br2	107.14 (2)	C2—N1—C2^{iii}	105.9 (4)
Br2^{i}—Ag1—Br1	112.947 (7)	N1—C1—H1A	109.5
Br2—Ag1—Br1	112.947 (7)	N1—C1—H1B	109.5
Br2^{i}—Ag1—Br1^{ii}	112.947 (7)	H1A—C1—H1B	109.5
Br2—Ag1—Br1^{ii}	112.947 (7)	N1—C1—H1C	109.5
Br1—Ag1—Br1^{ii}	97.93 (2)	H1A—C1—H1C	110.5
Br2^{i}—Ag1—Ag1^{i}	53.571 (11)	H1B—C1—H1C	108.5
Ag1—Br1—Ag1^{ii}	82.07 (2)	N1—C2—H2A	109.5
Ag1^{i}—Br2—Ag1	72.86 (2)	N1—C2—H2B	109.5
C1—N1—C1^{iii}	111.8 (4)	H2A—C2—H2B	109.5
C1—N1—C2	109.76 (13)	N1—C2—H2C	109.5
C1^{iii}—N1—C2	109.76 (13)	H2A—C2—H2C	109.5
C1—N1—C2^{iii}	109.76 (13)	H2B—C2—H2C	109.5
C1^{iii}—N1—C2^{iii}	109.76 (13)		
Br2^{i}—Ag1—Br1—Ag1^{ii}	−119.104 (11)	Br2^{i}—Ag1—Br2—Ag1^{i}	0.0
Br2—Ag1—Br1—Ag1^{ii}	119.104 (11)	Br1—Ag1—Br2—Ag1^{i}	125.005 (12)
Br1^{ii}—Ag1—Br1—Ag1^{ii}	0.0	Br1^{ii}—Ag1—Br2—Ag1^{i}	−125.005 (12)
Ag1^{i}—Ag1—Br1—Ag1^{ii}	180.0		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+1, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2C···Br1^{iv}	0.96	2.85	3.802 (4)	172

Symmetry codes: (iv) *x*+1/2, −*y*+3/2, −*z*+1/2.

Fig. 1

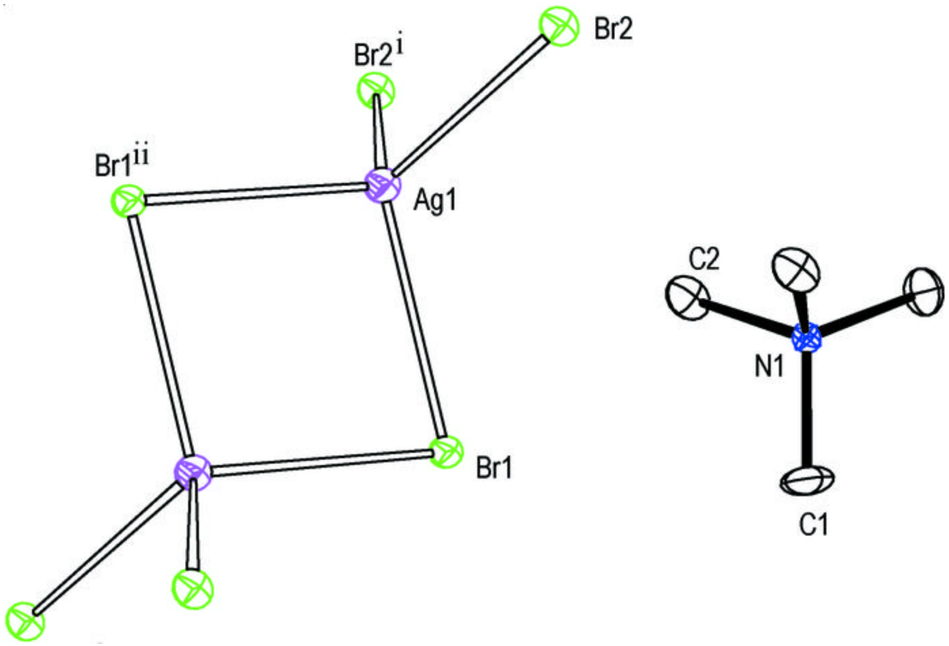

Fig. 2