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Poly[3,3′-diethyl-1,1′-(ethane-1,2-diyl)-diimidazolium [tetra-μ-bromido-diargentate(I)]]

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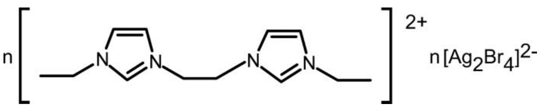
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.009 Å; R factor = 0.031; wR factor = 0.077; data-to-parameter ratio = 17.5.

The asymmetric unit of the title salt, $\{(C_{12}H_{20}N_4)[Ag_2Br_4]\}_n$, contains one-half of a substituted imidazolium cation, one Ag^+ and two Br^- ions. The cation is completed by crystallographic inversion symmetry. The crystal structure is made up from polymeric sheets of $\{[AgBr_2]^-\}_n$ anions extending parallel to (100). The basic building unit of the anion is a slightly distorted $AgBr_4$ tetrahedron. A four- and 12-membered ring system is formed by corner sharing of the $AgBr_4$ tetrahedra. The imidazolium cations are located between the anionic sheets and partly protrude into the voids defined by the 12-membered rings.

Related literature

For general background to *N*-heterocyclic carbenes, see: Arnold (2002); Lin & Vasam (2004). For related structures, see: Lee *et al.* (2002); Helgesson & Jagner (1990, 1991); Olson *et al.* (1994).



Experimental

Crystal data

$(C_{12}H_{20}N_4)[Ag_2Br_4]$
M_r = 755.90
Monoclinic, $P2_1/c$
a = 9.5593 (13) Å
b = 12.9512 (17) Å
c = 8.4565 (11) Å
β = 106.294 (2)°
V = 1004.9 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 9.90 mm^{-1}
T = 296 K
0.25 × 0.24 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2006)
T_{min} = 0.191, T_{max} = 0.219
5036 measured reflections
1766 independent reflections
1533 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.077
S = 1.06
1766 reflections
101 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.88 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ag1—Br1	2.6788 (7)	Ag1—Br1^{ii}	2.6999 (7)
Ag1—Br2^{i}	2.6934 (8)	Ag1—Br2	2.7227 (8)
Br1—Ag1—Br2^{i}	114.34 (3)	Br1—Ag1—Br2	119.16 (3)
Br1—Ag1—Br1^{ii}	103.92 (2)	Br2^{i}—Ag1—Br2	95.81 (2)
Br2^{i}—Ag1—Br1^{ii}	116.12 (3)	Br1^{ii}—Ag1—Br2	107.93 (2)

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

Data collection: *SMART* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Crystal Impact, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2354).

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supplementary materials

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Poly[3,3'-diethyl-1,1'-(ethane-1,2-diyl)diimidazolium [tetra-μ-bromido-diargentate(I)]]

Z. Wang, S. Liu and N. Zhang

Comment

Silver and other transition metal N-heterocyclic carbene complexes have played an important role in the development of metal-carbene systems for transmetalation reactions. Silver oxide is the most commonly used metal base for this purposes. Recent reviews dealing with silver N-heterocyclic carbenes were published by Arnold (2002) and Lin & Vasam (2004). The products differ depending upon reaction conditions and the imidazolium salt used. The silver carbene [Ag_2(Me_2-edimy)Cl_2] has been successfully synthesized by the reaction of [Me_2-edimyH_2][PF_6]$_2$ with Ag_2O in CH_3CN and [NM_4]Cl (Lee *et al.*, 2002). In an attempt to prepare a similar carbene, we obtained the title compound, $[(C_{12}H_{20}N_4)]^{2+}[Ag_2Br_4]^{2-}$, instead. Synthesis and crystal structure are reported in this article.

The crystal structure of the title salt is composed of $[(C_{12}H_{20}N_4)]^{2+}$ cations and $[Ag_2Br_4]^{2-}$ anions (Fig. 1). The anion forms polymeric sheets extending parallel to (100). The cations are located between the sheets and partly reach through the voids of the anion. A characteristic feature of the polymeric $\{[Ag_2Br_4]^{2-}\}_n$ anion is the construction of rings built up from corner-sharing of slightly distorted $AgBr_4$ tetrahedra. A large twelve-membered ring is formed by six alternating bromine and six silver atoms; another four-membered ring completes the building units of the polymeric anion (Fig. 2). The four-membered ring is very similar to that in the complex anion $[Ag_4Br_8]^{4-}$ (Helgesson & Jagner, 1991). These anions contain tetrahedrally coordinated Ag^+ atoms, whereas the $[Ag_4I_8]^{4-}$ ion, isolated as the tetraphenylphosphonium and tetraphenylarsonium salts, contains three-coordinated and four-coordinated Ag^+ (Helgesson & Jagner, 1990).

The average Ag—Br distance of the $AgBr_4$ tetrahedron in the title compound is 2.699 Å, which is considerably longer than for the $[Ag_2Br_4]^{2-}$ dimer ((2.518 (2) Å; Helgesson *et al.*, 1990). These values are comparable to other tetrahedral $AgBr_4$ units (Olson *et al.*, 1994).

Experimental

Ag_2O (2.32 g, 10 mmol) was added to a solution of 1H-imidazolium, 1,1'-(1,2-ethanediyl)bis[3-ethyl] dibromide (3.78 g, 10 mmol) in DMSO. This mixture was refluxed for 30 min under stirring, resulting in a clean solution. When the solvent was removed, the residue was exatracted with acetonitrile. The remaining residue was separated by centrifugation and the resulting solution was kept at room temperature. Colourless crystals of the title compound were obtained after slow evaporation (2.64 g, 34.9 % yield). Mp: 421 K. ^{1}H NMR ($CDCl_3$): 9.48(m,1H), 9.43 (m.1H), 6.84 (s, 2H, CH), 6.87 (s, 2H, CH), 4.52 (s, 4H, CH**2**), 3.64(s, 4H, CH**3**),1.42(m, 6H) ppm. Anal. calcd.: C, 19.05 H, 2.65; N, 7.41; found: C, 19.26; H, 2.57 ; N, 7.32%.

Refinement

The H atoms attached to C atoms of the imidazole ring were positioned geometrically and allowed to ride on their parent atoms, with a C—H distance of 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Methylene and methyl H atoms were likewise positioned geometrically and refined as riding atoms, with C—H = 0.97 Å (methylene) and C—H = 0.96 Å (methyl) and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Figures

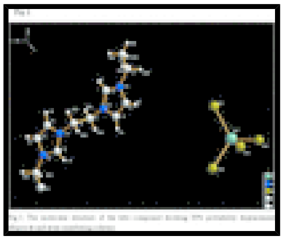

Fig. 1. The $[(C_{12}H_{20}N_4)]^{2+}$ cation and the basic $AgBr_4$ building unit of the polymeric anion. Displacement ellipsoids are drawn at the 30% probability level.

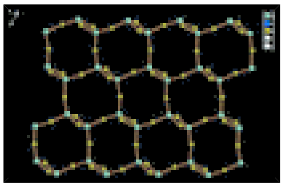

Fig. 2. The four- and twelve-membered ring system of the polymeric $\{[Ag_2Br_4]^{2-}\}_n$ anion.

Poly[3,3'-diethyl-1,1'-(ethane-1,2-diyl)diimidazolium [tetra-μ-bromido-diargentate(I)]]

Crystal data

$(C_{12}H_{20}N_4)[Ag_2Br_4]$
M_r = 755.90
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 9.5593 (13) Å
b = 12.9512 (17) Å
c = 8.4565 (11) Å
β = 106.294 (2)°
V = 1004.9 (2) Å^3
Z = 2

F(000) = 708
D_x = 2.498 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3112 reflections
θ = 2.2–27.8°
μ = 9.90 mm^{-1}
T = 296 K
Block, colourless
0.25 × 0.24 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
graphite
phi and ω scans
Absorption correction: multi-scan

1766 independent reflections
1533 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.023
$\theta_{\rm max}$ = 25.0°, $\theta_{\rm min}$ = 2.7°
h = −11→11

(*SADABS*; Sheldrick, 2006)	
$T_{\min} = 0.191$, $T_{\max} = 0.219$	$k = -15\rightarrow14$
5036 measured reflections	$l = -10\rightarrow5$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.077$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 1.7373P]$ where $P = (F_o^2 + 2F_c^2)/3$
1766 reflections	$(\Delta/\sigma)_{\max} = 0.001$
101 parameters	$\Delta\rho_{\max} = 0.64$ e Å^{-3}
0 restraints	$\Delta\rho_{\min} = -0.88$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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*	$U_{\rm iso}$*/$U_{\rm eq}$
Ag1	0.06806 (5)	0.63160 (3)	1.01898 (5)	0.05733 (16)
N1	0.8101 (4)	0.5496 (3)	0.4321 (5)	0.0424 (9)
N2	0.6179 (5)	0.6042 (4)	0.2519 (6)	0.0575 (12)
Br1	0.13558 (8)	0.75994 (4)	0.80302 (6)	0.0632 (2)
Br2	0.20441 (6)	0.44528 (4)	1.08097 (7)	0.05774 (18)
C1	0.6983 (6)	0.4833 (5)	0.4277 (8)	0.0646 (16)
H1	0.7040	0.4239	0.4911	0.078*
C2	0.5809 (6)	0.5178 (5)	0.3180 (8)	0.0650 (16)
H2	0.4889	0.4877	0.2912	0.078*
C3	0.7579 (6)	0.6221 (5)	0.3208 (7)	0.0584 (14)
H3	0.8110	0.6766	0.2952	0.070*
C4	0.5147 (8)	0.6630 (6)	0.1169 (10)	0.095 (3)
H4A	0.4988	0.6241	0.0153	0.114*
H4B	0.4219	0.6683	0.1417	0.114*
C5	0.5611 (12)	0.7605 (6)	0.0923 (13)	0.121 (4)

H5A	0.5711	0.8012	0.1898	0.182*
H5B	0.4911	0.7923	0.0012	0.182*
H5C	0.6535	0.7563	0.0688	0.182*
C6	0.9600 (5)	0.5390 (4)	0.5370 (6)	0.0432 (11)
H6A	0.9594	0.5169	0.6464	0.052*
H6B	1.0093	0.6052	0.5469	0.052*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.0590 (3)	0.0526 (3)	0.0561 (3)	−0.0056 (2)	0.0091 (2)	0.00076 (18)
N1	0.031 (2)	0.048 (2)	0.045 (2)	−0.0008 (18)	0.0046 (17)	0.0031 (18)
N2	0.039 (3)	0.074 (3)	0.053 (3)	0.005 (2)	0.002 (2)	0.013 (2)
Br1	0.1030 (5)	0.0489 (3)	0.0362 (3)	−0.0160 (3)	0.0171 (3)	0.0008 (2)
Br2	0.0326 (3)	0.0547 (3)	0.0783 (4)	0.0051 (2)	0.0029 (2)	−0.0090 (3)
C1	0.039 (3)	0.058 (3)	0.088 (4)	−0.008 (3)	0.002 (3)	0.023 (3)
C2	0.035 (3)	0.068 (4)	0.083 (4)	−0.006 (3)	0.002 (3)	0.014 (3)
C3	0.045 (3)	0.068 (4)	0.061 (4)	−0.005 (3)	0.013 (3)	0.017 (3)
C4	0.064 (5)	0.106 (6)	0.096 (6)	0.003 (4)	−0.007 (4)	0.043 (5)
C5	0.135 (9)	0.067 (5)	0.125 (8)	0.012 (5)	−0.026 (6)	0.003 (5)
C6	0.035 (3)	0.051 (3)	0.040 (3)	−0.004 (2)	0.005 (2)	−0.008 (2)

Geometric parameters (Å, °)

Ag1—Br1	2.6788 (7)	C2—H2	0.9300
Ag1—Br2^{i}	2.6934 (8)	C3—H3	0.9300
Ag1—Br1^{ii}	2.6999 (7)	C4—C5	1.374 (10)
Ag1—Br2	2.7227 (8)	C4—H4A	0.9700
N1—C3	1.324 (6)	C4—H4B	0.9700
N1—C1	1.363 (7)	C5—H5A	0.9600
N1—C6	1.466 (6)	C5—H5B	0.9600
N2—C3	1.321 (7)	C5—H5C	0.9600
N2—C2	1.341 (7)	C6—C6^{iii}	1.506 (9)
N2—C4	1.491 (8)	C6—H6A	0.9700
C1—C2	1.317 (8)	C6—H6B	0.9700
C1—H1	0.9300		
Br1—Ag1—Br2^{i}	114.34 (3)	N2—C3—H3	125.6
Br1—Ag1—Br1^{ii}	103.92 (2)	N1—C3—H3	125.6
Br2^{i}—Ag1—Br1^{ii}	116.12 (3)	C5—C4—N2	114.4 (7)
Br1—Ag1—Br2	119.16 (3)	C5—C4—H4A	108.7
Br2^{i}—Ag1—Br2	95.81 (2)	N2—C4—H4A	108.7
Br1^{ii}—Ag1—Br2	107.93 (2)	C5—C4—H4B	108.7
C3—N1—C1	106.9 (4)	N2—C4—H4B	108.7
C3—N1—C6	127.3 (4)	H4A—C4—H4B	107.6
C1—N1—C6	125.7 (4)	C4—C5—H5A	109.5
C3—N2—C2	108.4 (5)	C4—C5—H5B	109.5
C3—N2—C4	128.2 (5)	H5A—C5—H5B	109.5

C2—N2—C4	123.4 (5)	C4—C5—H5C	109.5
Ag1—Br1—Ag1^{iv}	152.39 (4)	H5A—C5—H5C	109.5
Ag1^{i}—Br2—Ag1	84.19 (2)	H5B—C5—H5C	109.5
C2—C1—N1	108.1 (5)	N1—C6—C6^{iii}	109.6 (5)
C2—C1—H1	125.9	N1—C6—H6A	109.8
N1—C1—H1	125.9	C6^{iii}—C6—H6A	109.8
C1—C2—N2	107.8 (5)	N1—C6—H6B	109.8
C1—C2—H2	126.1	C6^{iii}—C6—H6B	109.8
N2—C2—H2	126.1	H6A—C6—H6B	108.2
N2—C3—N1	108.8 (5)		
Br2^{i}—Ag1—Br1—Ag1^{iv}	4.51 (7)	C4—N2—C2—C1	177.1 (7)
Br1^{ii}—Ag1—Br1—Ag1^{iv}	−123.08 (5)	C2—N2—C3—N1	−1.2 (7)
Br2—Ag1—Br1—Ag1^{iv}	116.83 (6)	C4—N2—C3—N1	−177.9 (7)
Br1—Ag1—Br2—Ag1^{i}	−122.09 (3)	C1—N1—C3—N2	1.7 (7)
Br2^{i}—Ag1—Br2—Ag1^{i}	0.0	C6—N1—C3—N2	179.7 (5)
Br1^{ii}—Ag1—Br2—Ag1^{i}	119.87 (3)	C3—N2—C4—C5	−18.3 (12)
C3—N1—C1—C2	−1.5 (7)	C2—N2—C4—C5	165.6 (8)
C6—N1—C1—C2	−179.6 (5)	C3—N1—C6—C6^{iii}	−98.5 (7)
N1—C1—C2—N2	0.8 (8)	C1—N1—C6—C6^{iii}	79.1 (7)
C3—N2—C2—C1	0.2 (8)		

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

Fig. 1

Fig 1

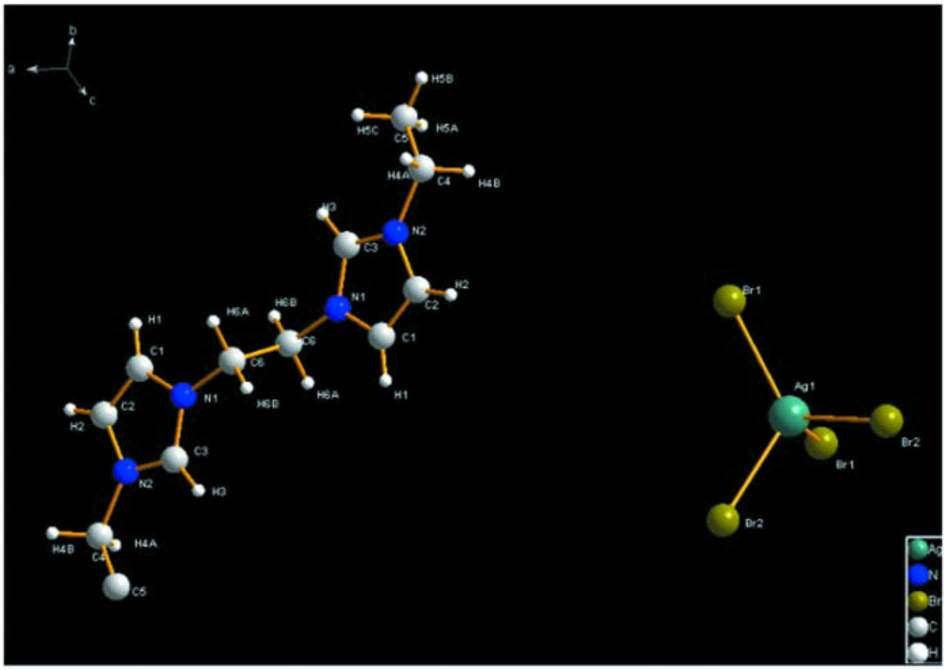

Fig.1. The molecular structure of the title compound showing 30% probability displacement ellipsoids and atom-numbering scheme.

Fig. 2