Short Communication

Crystal Structure of Tetramethylammonium *catena*-μ_4-bromo-di-μ-bromo-diargentate(I), $[N(CH_3)_4][Ag_2Br_3]$

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The configurations in the solid state assumed by halocuprates(I) crystallizing with symmetrical tetraalkylammonium and related cations appear to be determined by the degree of dilution imposed on the ligands by the cations.[1,2] The anions in tetraalkylammonium iodoargentates(I) and in the ammonium counterpart seem to follow a similar trend, i.e., $[N(C_4H_9)_4][Ag_3I_4]$,[3] $[N(CH_3)_4][Ag_2I_3]$,[4] $[N(CH_3)_4][AgI_2]$,[5] and $[NH_4]_2[AgI_3]$,[6] all the anionic species in these compounds being infinite chains containing four-coordinated silver(I). As part of an investigation of the anionic configurations assumed by bromoargentates(I) crystallizing with symmetrical tetraalkylammonium cations, the crystal structure of $[N(CH_3)_4][Ag_2Br_3]$ has been determined.

The compound was prepared according to the method of Kuhn & Schretzmann[7] for $[N(CH_3)_4][AgBr_2]$ and was recrystallized from dimethylformamide, colourless needles of $[N(CH_3)_4][Ag_2Br_3]$ being obtained. Crystals of tetramethylammonium *catena*-μ_4-bromo-di-μ-bromo-diargentate(I), $[N(CH_3)_4][Ag_2Br_3]$, M_r = 529.6, are orthorhombic, space group *Pnma* (No. 62),[8a] with a = 17.036(3), b = 7.0356(9), c = 9.702(1) Å, Z = 4, D_c = 3.02 g cm^{-3} and μ(Mo$K\alpha$) = 13.5 mm^{-1}.

Diffracted intensities from a crystal, 0.06×0.15×0.07 mm, were measured at approximately 290 °K for 3.5 ≤ 2θ ≤ 50.0° with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo$K\alpha$ radiation and the ω-2θ scan mode with a variable 2θ scan rate of 1.3–5.0° min^{-1}. A 96-step profile was recorded for each reflection and the Lehmann & Larsen[9] profile analysis method was used to calculate the intensities.[10] Of the 1125 independent reflections measured, excluding those systematically absent, 698 had $I > 3.0\ \sigma(I)$ and were used in the subsequent calculations. Correction was made for Lorentz and polarization effects; an empirical correction[11] for the effects of absorption was made after solution of the structure. The unit cell dimensions were determined from a Guinier-Hägg powder photograph [Cu$K\alpha_1$ radiation; KCl as internal standard (a = 6.2929 Å)], 81 reflections being used in the least-squares refinement of the unit cell parameters.

Tetramethylammonium *catena*-μ_4-bromo-di-μ-bromo-diargentate(I) is isostructural with $[N(CH_3)_4][Cu_2Cl_3]$,[2] and with $[N(CH_3)_4][Ag_2I_3]$,[4] and practically isostructural with $[C_6H_8N][Cu_2I_3]$.[12] Full-matrix least-squares refinement[13] of positional, isotropic and, subsequently, anisotropic thermal parameters gave R = 0.044 for 55

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[N(CH_3)_4][Ag_2Br_3]$. B_{eq} is defined as

$$\frac{8\pi^2}{3}\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

Estimated standard deviations are given in parentheses

Atom	x	y	z	B_{eq}
Ag	0.07826(7)	0.4994(2)	0.4207(1)	5.65(4)
Br(1)	−0.0477(1)	0.2500	0.3610(2)	3.60(5)
Br(2)	0.0992(2)	0.7500	0.2219(2)	5.28(7)
Br(3)	0.1853(1)	0.2500	0.4871(3)	5.12(7)
N	0.1509(8)	0.2500	−0.040(2)	3.4(4)
C(1)	0.215(2)	0.2500	0.062(3)	6.9(9)
C(2)	0.075(1)	0.2500	0.044(3)	6.9(9)
C(3)	0.149(1)	0.081(3)	−0.128(2)	7.1(6)

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parameters and 698 reflections. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*[8b] and weights were calculated according to $w = (40 + |F_o| + 0.002\,|F_o|^2)^{-1}$. A final difference map[13] showed a maximum residual electron density of 0.96 e Å^{-3}. The hydrogen atoms were not located. Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table 1. Structure factors and anisotropic thermal parameters may be obtained from the authors.

Discussion

In tetramethylammonium *catena*-μ_4-bromo-di-μ-bromo-diargentate(I), the anion is an infinite double chain of edge-sharing Ag(I)-Br tetrahedra (Fig. 1), similar to the anions in, e.g., $[N(CH_3)_4][Ag_2I_3]$,[4] $Cs[Ag_2I_3]$,[15] $Cs[Cu_2Cl_3]$,[15] $Cs[Cu_2I_3]$,[16] $[N(CH_3)_4][Cu_2Cl_3]$,[2] $[C_6H_8N][Cu_2I_3]$,[12] and

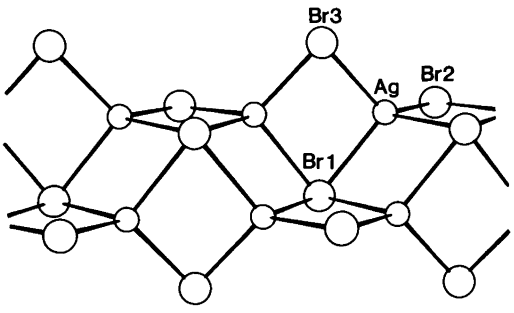

Fig. 1. Part of the infinite $[Ag_2Br_3]^-$ chain[14] showing the atomic numbering.

Table 3. Interatomic distances (Å) and angles (°) within the tetramethylammonium ion; estimated standard deviations are given in parentheses; symmetry code: (ii): $x, \frac{1}{2}-y,z$

N–C(1)	1.47(3)	C(1)–N–C(2)	105(2)
N–C(2)	1.53(3)	C(1)–N–C(3)	114(1)
N–C(3)	1.46(2)	C(2)–N–C(3)	107(1)
		C(3)–N–C(3^{ii})	109(2)

$[S(CH_3)_3][Cu_2I_3]$.[17] As in these compounds,[2,4,12,15–17] there are two sets of metal(I)-halide distances (Table 2), the shorter involving the μ_2-bromide ligands and the longer the μ_4. The Ag–Br distances in the infinite single chain of edge-sharing Ag(I)–Br tetrahedra in bis(ethylenediamine)nickel(II) dibromoargentate(I)[18] are intermediate between the two sets of distances in the present compound.

The interatomic angles within the $[Ag_2Br_3]^-$ anion are in close agreement with e.g., the values obtained for $[Cu_2Cl_3]^-$ in $[N(CH_3)_4][Cu_2Cl_3]$.[2] As in the related anions (*cf.* Refs 2, 12, 17), the metal···metal separation perpendicular to the length of the $[Ag_2Br_3]^-$ chain is slightly shorter than the corresponding separations along the length of the chain (Table 2).

A stereoscopic drawing illustrating the structure of $[N(CH_3)_4][Cu_2Cl_3]$, with which $[N(CH_3)_4][Ag_2Br_3]$ is isostructural, is to be found in Ref. 2. Bond distances and angles within the cation are given in Table 3. The shortest silver(I)···carbon distance is Ag···C(2) = 4.06(3) Å, while the closest distances between bromide and carbon are:

Table 2. Interatomic distances (Å) and angles (°) within the $[Ag_2Br_3]^-$ anion. Estimated standard deviations are given in parentheses. Symmetry code: (i): $\bar{x}, 1-y, 1-z$; (ii): $x, \frac{1}{2}-y,z$; (iii): $x, 1\frac{1}{2}-y,z$; (iv):$\bar{x}, y-\frac{1}{2}, 1-z$

Ag–Br(1)	2.833(2)	Ag···Ag^{i}	3.078(3)
Ag–Br(1^{i})	2.804(2)	Ag···Ag^{ii}	3.510(3)
Ag–Br(2)	2.638(2)	Ag···Ag^{iii}	3.526(3)
Ag–Br(3)	2.612(2)		
Br(1)–Ag–Br(1^{i})	113.80(5)	Ag –Br(1)–Ag^{iv}	112.06(7)
Br(1)–Ag–Br(2)	111.52(8)	Ag –Br(1)–Ag^{i}	66.20(5)
Br(1)–Ag–Br(3)	99.40(6)	Ag –Br(1)–Ag^{ii}	76.57(7)
Br(1^{i})–Ag–Br(2)	99.05(6)	Ag^{iv}–Br(1)–Ag^{i}	77.92(7)
Br(1^{i})–Ag–Br(3)	111.45(8)	Ag –Br(2)–Ag^{iii}	83.87(9)
Br(2)–Ag–Br(3)	122.35(9)	Ag –Br(3)–Ag^{ii}	84.43(9)

Br(1)···C(3^{v}) and Br(1)···C(3^{vi}) = 3.67(2) Å, Br(1)···C(2) = 3.72(3) Å, and Br(3)···C(3^{vii}) and Br(3)···C(3^{viii}) = 3.83(2) Å [symmetry code: (v): $\bar{x}, \frac{1}{2}+y, \bar{z}$; (vi): $\bar{x}\bar{y}\bar{z}$; (vii): $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$; (viii): $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$].

As expected, owing to the relatively small size of the cation, the present compound contains a polymeric bromoargentate(I) anion composed of shared Ag(I)–Br tetrahedra. This also reflects the greater tendency of silver(I), as compared with copper(I), to attain four coordination, a discrete $[Cu_2Br_5]^{3-}$ anion containing trigonal-planar coordinated copper(I) having been obtained with tetramethylammonium as cation.[19]

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