

Fourier synthesis  $0.55 \text{ e } \text{Å}^{-3}$ . No extinction correction.  $R = 0.068$  for the complete set of 4731 reflexions.\* Scattering factors for neutral atoms and  $f'$ ,  $f''$  from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer: MicroVAX II.

**Discussion.** The framework is built up of stacks of  $\text{H}_2\text{AsO}_4^-$  anions,  $\text{C}_7\text{H}_8\text{NO}_2^+$  cations and water molecules [Figs. 1 and 2; *STRUPLO84* (Fischer, 1985)]. Two separate lines of  $\text{H}_2\text{AsO}_4^-$  tetrahedra run along a plane parallel to  $bc$ . In each line,  $\text{H}_2\text{AsO}_4^-$  tetrahedra are bonded together through  $\text{O}(4)–\text{H}(4) \cdots \text{O}(2)$  bridges. The two adjacent lines are bridged by water molecules  $\text{O}(7)$ . The  $(\text{H}_2\text{AsO}_4^-)–\text{H}_2\text{O}–(\text{H}_2\text{AsO}_4^-)$  anionic framework extends in a plane parallel to  $bc$  and forms a thick layer of tetrahedra. The 4-carboxyanilinium groups connect two anionic layers of tetrahedra through hydrogen bonds of the  $\text{NH}_3^+$  and

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51212 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

*Acta Cryst.* (1988). **C44**, 2059–2062

## Tetraethylammonium *catena*- $\mu_4$ -Chloro-di- $\mu$ -chloro-diargentate(I) and Tetraethylammonium *catena*- $\mu_4$ -Bromo-di- $\mu$ -bromo-diargentate(I)

BY GÖRAN HELGESSON AND SUSAN JAGNER\*

*Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden*

(Received 15 June 1988; accepted 11 July 1988)

**Abstract.**  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Ag}_2\text{Cl}_3]$ ,  $M_r = 452.4$ , orthorhombic,  $Pnma$ ,  $a = 20.773$  (5),  $b = 11.895$  (3),  $c = 16.683$  (3) Å,  $V = 4122$  (2) Å<sup>3</sup>,  $Z = 12$ ,  $D_x = 2.19 \text{ Mg m}^{-3}$ ,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 3.38 \text{ mm}^{-1}$ ,  $F(000) = 2640$ ,  $T = 290 \text{ K}$ ,  $R = 0.047$  for 2310 unique observed [ $I \geq 3\sigma(I)$ ] reflections and 311 parameters.  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Ag}_2\text{Br}_3]$ ,  $M_r = 585.7$ , orthorhombic,  $Pnma$ ,  $a = 21.161$  (7),  $b = 12.207$  (3),  $c = 17.208$  (4) Å,  $V = 4445$  (2) Å<sup>3</sup>,  $Z = 12$ ,  $D_x = 2.63 \text{ Mg m}^{-3}$ ,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 10.6 \text{ mm}^{-1}$ ,  $F(000) = 3288$ ,  $T = 290 \text{ K}$ ,  $R = 0.062$  for 2964 unique observed [ $I \geq 3\sigma(I)$ ] reflections and 311 parameters. Both compounds contain infinite double-chain anions composed of edge-sharing silver(I) halide tetrahedra. Ag–Cl distances range from 2.514 (2) to 2.778 (2) Å

and Ag–Br distances from 2.630 (2) to 2.844 (2) Å. The Ag $\cdots$ Ag contacts are 3.348 (2)–3.486 (2) Å and 3.250 (3)–3.547 (2) Å in  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Ag}_2\text{Cl}_3]$  and  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Ag}_2\text{Br}_3]$ , respectively.

carboxylic groups. As in the previous structure we observe a layer structure with planes of anions separated from planes of cations. The anionic arrangement is near that described for  $(\text{H}_2\text{PO}_4^-, \text{H}_2\text{O}, \text{H}_2\text{PO}_4^-)$  in  $\text{N}(\text{CH}_3)_4\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  material (Ohama, Machida, Nakamura & Kunifujii, 1987).

Tables 1 and 2 report the final atomic coordinates and the main interatomic distances.

### References

- Enraf–Nonius (1977). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.  
FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
MAIN, P., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
OHAMA, N., MACHIDA, M., NAKAMURA, T. & KUNIFUJI, Y. (1987). *Acta Cryst.* **C43**, 962–964.  
TORDJMAN, I., MASSE, R. & GUITEL, J. C. (1988). *Acta Cryst.* **C44**, 2055–2057.

\* To whom correspondence should be addressed.

Kildea, Skelton & White, 1986), occurs in [N(CH<sub>3</sub>)<sub>4</sub>][Ag<sub>2</sub>Br<sub>3</sub>] (Jagner, Olson & Stomberg, 1986), and a single chain of edge-sharing silver(I) chloride tetrahedra in [N(CH<sub>3</sub>)<sub>4</sub>][AgCl<sub>2</sub>] (Helgesson, Josefsson & Jagner, 1988). Discrete dinuclear [Ag<sub>2</sub>X<sub>4</sub>]<sup>2-</sup> species, X = Cl or Br, in which Ag<sup>I</sup> exhibits distorted trigonal-planar coordination geometry, have been isolated with the tetraphenylphosphonium cation (Helgesson & Jagner, 1988). Far-infrared spectroscopic studies on tetraethylammonium chloroargentate(I) and tetraethylammonium bromoargentate(I) indicate the presence of infinite chain anions of stoichiometry [Ag<sub>2</sub>X<sub>3</sub>]<sup>-</sup> (Bottger & Geddes, 1967). As part of an investigation of the dependence of the coordination of Ag<sup>I</sup> in haloargentates(I) on cation size, the crystal structures of these compounds have been determined, the results being presented in this communication.

**Experimental.** [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>][Ag<sub>2</sub>Cl<sub>3</sub>] (1) was prepared under nitrogen according to the method of Bowmaker, Clark, Rogers, Camus & Marsich (1984), using 0.50 g (3.5 mmol) AgCl (ICN Biomedicals, K. & K), 0.58 g (3.5 mmol) tetraethylammonium chloride (Merck) and 25 ml acetonitrile. Colourless elongated prisms, m.p. 479–480 K, were deposited on slow cooling of the solution from 353 K to ambient temperature. [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>][Ag<sub>2</sub>Br<sub>3</sub>] (2) was prepared in an analogous manner from 0.50 g (2.7 mmol) AgBr (ICN Biomedicals, K. & K), 0.56 g (2.7 mmol) tetraethylammonium bromide (Merck) and 20 ml dimethylformamide, colourless elongated prisms, m.p. 498–499 K, being obtained on slow cooling of the solution from 423 K to ambient temperature. The use of acetonitrile as solvent in the preparation of (2) resulted in crystals of inferior quality. Preliminary unit-cell dimensions and space group from rotation and Weissenberg films, suggesting isostructurality of (1) and (2); rotation photographs about *a* indicated a pseudo *a*-axis length of approximately 7 Å, the presence of weak layer lines requiring a true *a* axis of three times this magnitude. Intensity data collected on a Syntex P2<sub>1</sub> diffractometer; graphite-monochromated Mo *K*<sub>α</sub> radiation; crystal dimensions (distance to faces from vertex chosen as origin for absorption correction) (1): 0.000 (100, 00 $\bar{1}$ , 011), 0.314 (100), 0.177 (0 $\bar{1}\bar{1}$ ), 0.141 (001), 0.106 (01 $\bar{1}$ ), 0.106 (0 $\bar{1}$ 1) mm; (2): 0.000 (10 $\bar{1}$ , 00 $\bar{1}$ , 01 $\bar{1}$ ), 0.217 (001), 0.168 (101), 0.181 (1 $\bar{0}$ 1), 0.252 (1 $\bar{0}$ 1), 0.230 (0 $\bar{1}$ 1) mm. 15 reflections used to determine unit-cell parameters; 3.5 ≤ 2θ ≤ 55°; (1): 0 ≤ *h* ≤ 27; 0 ≤ *k* ≤ 15; 0 ≤ *l* ≤ 21; (2): 0 ≤ *h* ≤ 27; 0 ≤ *k* ≤ 15; 0 ≤ *l* ≤ 22; ω–2θ scan mode, variable 2θ scan rate (1): 2.0–29.3°, (2): 2.0–15.0° min<sup>-1</sup>; 96-step profiles; Lehmann & Larsen (1974) profile-analysis method used to calculate the intensities (Lindqvist & Ljungström, 1979); variation in intensity of two standard reflections, measured every 48 reflections, <2% for (1), <6% for (2); (1): 4988 unique, non-systematically

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for the non-hydrogen atoms in [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>][Ag<sub>2</sub>Cl<sub>3</sub>] with e.s.d.'s in parentheses

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Ag(1)	8( <i>d</i> )	0.01172 (3)	0.10926 (6)	0.25063 (4)	4.81 (2)
Ag(2)	8( <i>d</i> )	0.17819 (3)	0.10836 (6)	0.26300 (4)	4.90 (2)
Ag(3)	8( <i>d</i> )	0.34520 (3)	0.10346 (6)	0.26333 (4)	4.60 (2)
Cl(1)	4( <i>c</i> )	0.1027 (1)	0.2500	0.1834 (1)	3.30 (7)
Cl(2)	4( <i>c</i> )	−0.0748 (1)	0.2500	0.3144 (2)	3.41 (7)
Cl(3)	8( <i>d</i> )	0.0901 (1)	0.0160 (2)	0.3466 (1)	4.45 (5)
Cl(4)	8( <i>d</i> )	−0.0667 (1)	0.0003 (2)	0.1638 (1)	5.24 (6)
Cl(5)	4( <i>c</i> )	0.2660 (1)	0.2500	0.3376 (2)	3.86 (7)
Cl(6)	8( <i>d</i> )	0.2597 (1)	−0.0065 (2)	0.1876 (1)	4.20 (5)
N(1)	4( <i>c</i> )	0.2690 (4)	−0.2500	0.4389 (4)	2.7 (2)
C(11)	4( <i>c</i> )	0.3366 (5)	−0.2500	0.4023 (6)	3.4 (3)
C(12)	4( <i>c</i> )	0.3390 (7)	−0.2500	0.3113 (7)	4.4 (4)
C(13)	4( <i>c</i> )	0.2773 (5)	−0.2500	0.5284 (6)	3.1 (3)
C(14)	4( <i>c</i> )	0.2162 (6)	−0.2500	0.5748 (7)	4.3 (3)
C(15)	8( <i>d</i> )	0.2318 (4)	−0.1473 (7)	0.4110 (4)	3.3 (2)
C(16)	8( <i>d</i> )	0.2583 (4)	−0.0363 (7)	0.4387 (5)	3.8 (2)
N(2)	4( <i>c</i> )	0.0853 (4)	−0.2500	0.0855 (5)	2.8 (2)
C(21)	4( <i>c</i> )	0.0187 (6)	−0.2500	0.0549 (9)	4.6 (4)
C(22)	4( <i>c</i> )	0.0145 (10)	−0.2500	−0.0347 (11)	7.8 (7)
C(23)	4( <i>c</i> )	0.0771 (6)	−0.2500	0.1782 (7)	4.0 (3)
C(24)	4( <i>c</i> )	0.1381 (8)	−0.2500	0.2268 (8)	6.2 (5)
C(25)	8( <i>d</i> )	0.1237 (4)	−0.1474 (7)	0.0610 (5)	4.2 (2)
C(26)	8( <i>d</i> )	0.0927 (5)	−0.0371 (8)	0.0796 (8)	5.0 (3)
N(3)	4( <i>c</i> )	0.4199 (4)	−0.2500	0.0565 (4)	3.0 (2)
C(31)	4( <i>c</i> )	0.4769 (5)	−0.2500	−0.0018 (6)	3.4 (3)
C(32)	4( <i>c</i> )	0.5424 (6)	−0.2500	0.0379 (8)	4.3 (4)
C(33)	4( <i>c</i> )	0.3614 (5)	−0.2500	0.0018 (6)	3.2 (3)
C(34)	4( <i>c</i> )	0.2967 (6)	−0.2500	0.0461 (8)	4.5 (4)
C(35)	8( <i>d</i> )	0.4206 (4)	−0.1481 (6)	0.1102 (4)	3.4 (2)
C(36)	8( <i>d</i> )	0.4180 (5)	−0.0354 (8)	0.0690 (6)	4.4 (3)

absent reflections measured, of which 2310 with  $I \geq 3\sigma(I)$ , (2): 5377 unique, non-systematically absent reflections measured, of which 2964 with  $I \geq 3\sigma(I)$ ; absorption correction *ABSORB* (DeTitta, 1985), transmission factors (1): 0.691–0.819, (2): 0.044–0.244. The coordinates of Ag and Cl in (1) were obtained from a Patterson map and those of the remaining atoms from successive electron-density maps. The coordinates of (1) were used as starting point for the refinement of (2). H atoms located from difference maps; non-hydrogen atoms refined with anisotropic thermal parameters and H atoms with isotropic thermal parameters set equal to the *B*<sub>eq</sub> values of the carrying C atoms and not refined; isotropic extinction parameters (Coppens & Hamilton, 1970) refined towards the end of the refinement; (1)  $g' = 1.9 (1) \times 10^{-1}$ , (2)  $g' = 3.0 (4) \times 10^{-2}$ . Full-matrix least-squares refinement based on *F* gave final *R* = 0.047 for (1) (2310 reflections; 311 parameters),  $wR = 0.057$ ,  $w = [\sigma^2(F_o) + 0.00055F_o^2]^{-1}$ ;  $(\Delta/\sigma)_{\text{max}} < 0.24$  for non-H; final difference electron density: max. 0.73, min. −2.01 e Å<sup>-3</sup>. Final *R* = 0.062 for (2) (2964 reflections; 311 parameters),  $wR = 0.070$ , weighting scheme as for (1);  $(\Delta/\sigma)_{\text{max}} < 0.55$  for non-H; final difference electron density: max. 1.02, min. −1.98 e Å<sup>-3</sup>. Anomalous-dispersion correction for all non-H atoms. Atomic scattering factors from

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for the non-hydrogen atoms in  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Ag}_2\text{Br}_3]$  with e.s.d.'s in parentheses

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

		x	y	z	$B_{\text{eq}}$
Ag(1)	8(d)	0.01406 (4)	0.11463 (8)	0.24729 (6)	4.79 (3)
Ag(2)	8(d)	0.18011 (4)	0.11688 (8)	0.26354 (6)	4.88 (3)
Ag(3)	8(d)	0.34764 (4)	0.10875 (8)	0.26264 (6)	4.74 (3)
Br(1)	4(c)	0.10390 (6)	0.2500	0.17329 (9)	3.12 (4)
Br(2)	4(c)	-0.07303 (6)	0.2500	0.32113 (10)	3.30 (4)
Br(3)	8(d)	-0.09170 (5)	0.01757 (8)	0.34550 (8)	4.33 (3)
Br(4)	8(d)	-0.06496 (5)	-0.00059 (11)	0.16130 (9)	5.51 (4)
Br(5)	4(c)	0.26816 (7)	0.2500	0.34527 (10)	3.58 (4)
Br(6)	8(d)	0.26143 (5)	-0.00303 (9)	0.18513 (8)	4.18 (3)
N(1)	4(c)	0.2692 (4)	-0.2500	0.4330 (7)	2.4 (3)
C(11)	4(c)	0.3348 (6)	-0.2500	0.4011 (9)	3.1 (4)
C(12)	4(c)	0.3373 (11)	-0.2500	0.3118 (12)	5.8 (7)
C(13)	4(c)	0.2754 (6)	-0.2500	0.5225 (9)	3.2 (4)
C(14)	4(c)	0.2154 (11)	-0.2500	0.5660 (16)	5.4 (7)
C(15)	8(d)	0.2311 (5)	-0.1500 (9)	0.4085 (6)	3.4 (3)
C(16)	8(d)	0.2576 (6)	-0.0415 (10)	0.4351 (8)	4.2 (3)
N(2)	4(c)	0.0902 (5)	-0.2500	0.0891 (7)	2.8 (3)
C(21)	4(c)	0.0238 (8)	-0.2500	0.0557 (14)	5.3 (6)
C(22)	4(c)	0.0206 (15)	-0.2500	-0.0289 (20)	10.5 (13)
C(23)	4(c)	0.0813 (9)	-0.2500	0.1773 (11)	4.6 (5)
C(24)	4(c)	0.1415 (17)	-0.2500	0.2239 (15)	6.9 (9)
C(25)	8(d)	0.1281 (5)	-0.1512 (9)	0.0626 (7)	3.9 (3)
C(26)	8(d)	0.0986 (6)	-0.0415 (10)	0.0812 (10)	4.8 (4)
N(3)	4(c)	0.4221 (5)	-0.2500	0.0575 (7)	3.0 (3)
C(31)	4(c)	0.4765 (6)	-0.2500	0.0028 (9)	2.9 (4)
C(32)	4(c)	0.5402 (8)	-0.2500	-0.0422 (13)	4.6 (6)
C(33)	4(c)	0.3630 (6)	-0.2500	0.0092 (9)	2.7 (4)
C(34)	4(c)	0.3016 (7)	-0.2500	0.0509 (13)	4.5 (6)
C(35)	8(d)	0.4225 (5)	-0.1505 (10)	0.1121 (7)	3.4 (3)
C(36)	8(d)	0.4199 (6)	-0.0417 (10)	0.0712 (9)	4.6 (4)

*International Tables for X-ray Crystallography* (1974). Computer programs described by Lindgren (1977) and Andersen (1985). Atomic coordinates for the non-hydrogen atoms are listed in Tables 1 and 2.\*

**Discussion.**  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Ag}_2\text{Cl}_3]$  and  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Ag}_2\text{Br}_3]$  are isostructural, both compounds containing double chains of edge-sharing tetrahedra of the type determined for  $[\text{N}(\text{CH}_3)_4][\text{Ag}_2\text{Br}_3]$  (Jagner, Olson & Stomberg, 1986) and  $[\text{N}(\text{CH}_3)_4][\text{Ag}_2\text{I}_3]$  (Meyer, 1963; Kildea, Skelton & White, 1986), confirming the structures predicted by Bottger & Geddes (1967) from far-IR spectra. The  $[\text{Ag}_2\text{Cl}_3]^-$  anion is depicted in Fig. 1 and interatomic distances and angles within  $[\text{Ag}_2\text{Cl}_3]^-$  and  $[\text{Ag}_2\text{Br}_3]^-$  are given in Tables 3 and 4, respectively. Although the  $[\text{Ag}_2\text{Br}_3]^-$  anion has been described previously, this would appear to be the first crystallographic determination of a double  $[\text{Ag}_2\text{Cl}_3]^-$  chain. The silver(I) chloride distances involving the  $\mu_2$  ligands Cl(3), Cl(4) and Cl(6) (Table 3) are all slightly shorter than those determined for the single chain of edge-

sharing tetrahedra in  $[\text{N}(\text{CH}_3)_4][\text{AgCl}_2]$ , viz. 2.599 (1) and 2.618 (1)  $\text{\AA}$  (Helgesson, Josefsson & Jagner, 1988), whereas those associated with the  $\mu_4$  bridges are somewhat longer. Similarly, there are seen to be two sets of silver(I) bromide distances in  $[\text{Ag}_2\text{Br}_3]^-$  (Table 4). This is a structural feature documented previously for this type of anion (*cf.* Kildea, Skelton & White, 1986; Jagner, Olson & Stomberg, 1986), the  $\mu_2$  Ag—Br distances in  $[\text{N}(\text{CH}_3)_4][\text{Ag}_2\text{Br}_3]$  being 2.612 (2) and 2.638 (2)  $\text{\AA}$  and the  $\mu_4$  2.804 (2) and 2.833 (2)  $\text{\AA}$ .

Perhaps the most unexpected aspect of the structures of these compounds is that the chains extend parallel to the *a* axis in *Pnma* which is tripled compared with the repeat distance found in analogous compounds. Apart from the  $[\text{N}(\text{CH}_3)_4][\text{Ag}_2\text{X}_3]$  salts mentioned previously (Meyer, 1963; Kildea, Skelton & White, 1986; Jagner, Olson & Stomberg, 1986), three halocuprate(I) analogues crystallize in this space group (Hartl & Mahdjour-Hassan-Abadi, 1984; Asplund, Jagner & Nilsson, 1985; Andersson & Jagner, 1986). The repeat distance is in all cases the *b* axial length [ $\approx 7$   $\text{\AA}$  in the haloargentates(I) and  $\approx 6.5$   $\text{\AA}$  in the halocuprates(I)], *i.e.* the chains extend along *b* with all the ligand atoms situated on crystallographic mirror planes. Most commonly *Z* = 4, but in  $[\text{S}(\text{CH}_3)_3][\text{Cu}_2\text{I}_3]$  (Asplund, Jagner & Nilsson, 1985) there are two crystallographically independent chains such that *Z* = 12; both chains extend along *b*, however. In the present compounds, only the  $\mu_4$  ligands are situated on crystallographic mirror planes, which lie in, instead of perpendicular to, the  $[\text{Ag}_2\text{X}_3]^-$  chains. The Cu...Cu separations perpendicular to the length of the  $[\text{Cu}_2\text{Cl}_3]^-$  (Andersson & Jagner, 1986) and  $[\text{Cu}_2\text{I}_3]^-$  (Hartl & Mahdjour-Hassan-Abadi, 1984; Asplund, Jagner & Nilsson, 1985) chains are all slightly shorter than the corresponding distances along the chains. In  $[\text{N}(\text{CH}_3)_4][\text{Ag}_2\text{Br}_3]$ , there is an analogous difference of approximately 0.5  $\text{\AA}$ , *i.e.* 3.078 (3)  $\text{\AA}$  (perpendicular) as opposed to 3.510 (3) and 3.526 (3)  $\text{\AA}$  (parallel) (Jagner, Olson & Stomberg, 1986). In the present compounds, and in  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Ag}_2\text{Cl}_3]$  in particular (Table 3), there

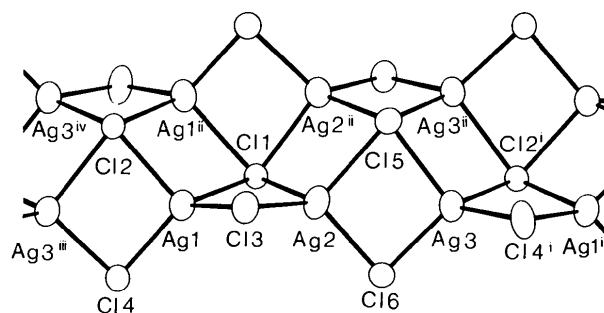


Fig. 1. The  $[\text{Ag}_2\text{Cl}_3]^-$  anion in  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Ag}_2\text{Cl}_3]$ , showing the atomic numbering; the  $[\text{Ag}_2\text{Br}_3]^-$  ion in  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Ag}_2\text{Br}_3]$  is analogous. The thermal ellipsoids enclose 50% probability (Johnson, 1965). For symmetry code see Table 3.

\* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters and bond distances and angles within the tetraethylammonium cations for both structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51234 (59 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Interatomic distances (Å) and angles (°) within the [Ag<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup> ion in (1) with e.s.d.'s in parentheses*Symmetry code: (i)  $\frac{1}{2} + x, y, \frac{1}{2} - z$ ; (ii)  $x, \frac{1}{2} - y, z$ ; (iii)  $x - \frac{1}{2}, y, \frac{1}{2} - z$ ; (iv)  $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$ .

Ag(1)—Cl(1)	2.763 (2)	Ag(3)—Cl(6)	2.542 (2)
Ag(1)—Cl(2)	2.676 (2)	Ag(3)—Cl(2 <sup>ii</sup> )	2.735 (2)
Ag(1)—Cl(3)	2.519 (2)	Ag(3)—Cl(4 <sup>i</sup> )	2.516 (2)
Ag(1)—Cl(4)	2.536 (2)	Ag(1)...Ag(1 <sup>ii</sup> )	3.348 (2)
Ag(2)—Cl(1)	2.658 (2)	Ag(2)...Ag(2 <sup>ii</sup> )	3.369 (2)
Ag(2)—Cl(3)	2.531 (2)	Ag(3)...Ag(3 <sup>ii</sup> )	3.486 (2)
Ag(2)—Cl(5)	2.778 (2)	Ag(1)...Ag(2)	3.464 (1)
Ag(2)—Cl(6)	2.514 (2)	Ag(2)...Ag(3)	3.470 (1)
Ag(3)—Cl(5)	2.698 (2)	Ag(3)...Ag(1)	3.468 (1)
Cl(1)—Ag(1)—Cl(2)	103.98 (5)	Ag(1)—Cl(1)—Ag(2)	79.42 (5)
Cl(1)—Ag(1)—Cl(3)	94.45 (7)	Ag(1)—Cl(1)—Ag(1 <sup>ii</sup> )	74.60 (7)
Cl(1)—Ag(1)—Cl(4)	121.13 (7)	Ag(2)—Cl(2)—Ag(1 <sup>ii</sup> )	125.78 (10)
Cl(2)—Ag(1)—Cl(3)	117.54 (8)	Ag(2)—Cl(1)—Ag(2 <sup>ii</sup> )	78.67 (7)
Cl(2)—Ag(1)—Cl(4)	96.62 (7)	Ag(1)—Cl(2)—Ag(1 <sup>ii</sup> )	77.44 (7)
Cl(3)—Ag(1)—Cl(4)	123.09 (8)	Ag(1)—Cl(2)—Ag(3 <sup>ii</sup> )	79.69 (5)
Cl(1)—Ag(2)—Cl(3)	96.76 (7)	Ag(1)—Cl(2)—Ag(3 <sup>iv</sup> )	128.18 (10)
Cl(1)—Ag(2)—Cl(5)	103.13 (6)	Ag(3 <sup>ii</sup> )—Cl(2)—Ag(3 <sup>iv</sup> )	79.17 (7)
Cl(1)—Ag(2)—Cl(6)	119.47 (7)	Ag(1)—Cl(3)—Ag(2)	86.62 (7)
Cl(3)—Ag(2)—Cl(5)	119.80 (8)	Ag(1)—Cl(4)—Ag(3 <sup>ii</sup> )	86.68 (7)
Cl(3)—Ag(2)—Cl(6)	121.34 (7)	Ag(2)—Cl(5)—Ag(3)	78.63 (8)
Cl(5)—Ag(2)—Cl(6)	96.39 (7)	Ag(2)—Cl(5)—Ag(2 <sup>ii</sup> )	74.67 (8)
Cl(5)—Ag(3)—Cl(6)	97.78 (7)	Ag(2)—Cl(5)—Ag(3 <sup>ii</sup> )	125.91 (10)
Cl(5)—Ag(3)—Cl(2)	100.16 (6)	Ag(3)—Cl(5)—Ag(3 <sup>ii</sup> )	80.50 (8)
Cl(5)—Ag(3)—Cl(4)	122.45 (8)	Ag(2)—Cl(6)—Ag(3)	86.66 (7)
Cl(6)—Ag(3)—Cl(2)	121.11 (7)		
Cl(6)—Ag(3)—Cl(4)	119.82 (7)		
Cl(2)—Ag(3)—Cl(4)	95.61 (7)		

Table 4. *Interatomic distances (Å) and angles (°) within the [Ag<sub>2</sub>Br<sub>3</sub>]<sup>-</sup> ion in (2) with e.s.d.'s in parentheses*

For symmetry code see Table 3.

Ag(1)—Br(1)	2.823 (2)	Ag(3)—Br(6)	2.640 (2)
Ag(1)—Br(2)	2.782 (2)	Ag(3)—Br(2)	2.805 (2)
Ag(1)—Br(3)	2.638 (3)	Ag(3)—Br(4 <sup>i</sup> )	2.630 (2)
Ag(1)—Br(4)	2.639 (2)	Ag(1)...Ag(1 <sup>ii</sup> )	3.305 (2)
Ag(2)—Br(1)	2.766 (2)	Ag(2)...Ag(2 <sup>ii</sup> )	3.250 (2)
Ag(2)—Br(3)	2.638 (2)	Ag(3)...Ag(3 <sup>ii</sup> )	3.449 (2)
Ag(2)—Br(5)	2.844 (2)	Ag(1)...Ag(2)	3.525 (2)
Ag(2)—Br(6)	2.631 (2)	Ag(2)...Ag(3)	3.547 (2)
Ag(3)—Br(5)	2.797 (2)	Ag(3)...Ag(1)	3.526 (2)
Br(1)—Ag(1)—Br(2)	107.72 (4)	Ag(1)—Br(1)—Ag(2)	78.19 (4)
Br(1)—Ag(1)—Br(3)	97.62 (5)	Ag(1)—Br(1)—Ag(1 <sup>ii</sup> )	71.67 (5)
Br(1)—Ag(1)—Br(4)	119.07 (6)	Ag(2)—Br(1)—Ag(1 <sup>ii</sup> )	118.89 (6)
Br(2)—Ag(1)—Br(3)	112.75 (6)	Ag(2)—Br(1)—Ag(2 <sup>ii</sup> )	71.95 (6)
Br(2)—Ag(1)—Br(4)	98.80 (5)	Ag(1)—Br(2)—Ag(1 <sup>ii</sup> )	72.87 (6)
Br(3)—Ag(1)—Br(4)	120.96 (6)	Ag(1)—Br(2)—Ag(3 <sup>ii</sup> )	78.27 (4)
Br(1)—Ag(2)—Br(3)	99.02 (5)	Ag(1)—Br(2)—Ag(3 <sup>iv</sup> )	121.79 (7)
Br(1)—Ag(2)—Br(5)	108.89 (4)	Ag(3 <sup>ii</sup> )—Br(2)—Ag(3 <sup>iv</sup> )	75.86 (6)
Br(1)—Ag(2)—Br(6)	114.84 (6)	Ag(1)—Br(3)—Ag(2)	83.84 (5)
Br(3)—Ag(2)—Br(5)	117.57 (6)	Ag(1)—Br(4)—Ag(3 <sup>ii</sup> )	84.03 (6)
Br(3)—Ag(2)—Br(6)	118.84 (5)	Ag(2)—Br(5)—Ag(3)	77.90 (4)
Br(5)—Ag(2)—Br(6)	98.22 (5)	Ag(2)—Br(5)—Ag(2 <sup>ii</sup> )	69.69 (6)
Br(5)—Ag(3)—Br(6)	99.20 (5)	Ag(2)—Br(5)—Ag(3 <sup>ii</sup> )	119.65 (7)
Br(5)—Ag(3)—Br(2)	104.01 (4)	Ag(3)—Br(5)—Ag(3 <sup>ii</sup> )	76.12 (6)
Br(5)—Ag(3)—Br(4)	118.87 (6)	Ag(2)—Br(6)—Ag(3)	84.57 (5)
Br(6)—Ag(3)—Br(2)	118.14 (6)		
Br(6)—Ag(3)—Br(4)	118.37 (6)		
Br(2)—Ag(3)—Br(4)	98.45 (5)		

would, however, seem to be little or no systematic difference between the magnitudes of the Ag...Ag separations parallel and perpendicular to the chains.

The cations show no abnormal features apart from somewhat large thermal parameters for some of the  $\beta$ -carbon atoms, e.g. C(22), presumably indicating slight disorder. This atom is involved in a short non-bonded contact to the [Ag<sub>2</sub>X<sub>3</sub>]<sup>-</sup> chain, i.e. Cl(1)...C(22<sup>v</sup>) = 3.48 (2) Å in [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>][Ag<sub>2</sub>Cl<sub>3</sub>] and Br(1)...C(22<sup>v</sup>) = 3.62 (3) Å in [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>][Ag<sub>2</sub>Br<sub>3</sub>]. Cl(1) and Br(1) each exhibit one additional very short cation contact, viz. Cl(1)...C(13<sup>vi</sup>) = 3.59 (1) and Br(1)...C(13<sup>vi</sup>) = 3.64 (2) Å, respectively, there being several other halide-carbon contacts marginally longer than these values [symmetry code: (v)  $-x, -y, -z$ ; (vi)  $\frac{1}{2} - x, -y, z - \frac{1}{2}$ ].

Financial support from the Swedish Natural Science Research Council (NFR) is gratefully acknowledged.

## References

- ANDERSEN, L. (1985). *Structure Determination of Some Symmetrical Oxoanions of Sulfur(IV), Selenium(IV) and Tellurium(IV) and Implementation of a General Set of Programs for Crystallographic Computing*. Thesis, Department of Inorganic Chemistry, Chalmers Univ. of Technology and Univ. of Göteborg, Göteborg, Sweden.
- ANDERSSON, S. & JAGNER, S. (1986). *Acta Chem. Scand. Ser. A*, **40**, 177–181.
- ASPLUND, M., JAGNER, S. & NILSSON, M. (1985). *Acta Chem. Scand. Ser. A*, **39**, 447–451.
- BOTTGER, G. L. & GEDDES, A. L. (1967). *Spectrochim. Acta Part A*, **23**, 1551–1559.
- BOWMAKER, G. A., CLARK, G. R., ROGERS, D. A., CAMUS, A. & MARSICH, N. (1984). *J. Chem. Soc. Dalton Trans.* pp. 37–45.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- DETTITA, G. T. (1985). *J. Appl. Cryst.* **18**, 75–79.
- GELLER, S. & LIND, M. D. (1970). *J. Chem. Phys.* **52**, 5854–5861.
- GILMORE, C. J., TUCKER, P. A. & WOODWARD, P. (1971). *J. Chem. Soc. A*, pp. 1337–1341.
- HARTL, H. & MAHDJOUR-HASSAN-ABADI, F. (1984). *Z. Naturforsch. Teil B*, **39**, 149–156.
- HELGESSION, G. & JAGNER, S. (1988). *J. Chem. Soc. Dalton Trans.* pp. 2117–2120.
- HELGESSION, G., JOSEFSSON, M. & JAGNER, S. (1988). *Acta Cryst.* **C44**, 1729–1731.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JAGNER, S., OLSON, S. & STOMBERG, R. (1986). *Acta Chem. Scand. Ser. A*, **40**, 230–232.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KILDEA, J. D., SKELTON, B. W. & WHITE, A. H. (1986). *Aust. J. Chem.* **39**, 171–175.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- LINDGREN, O. (1977). *An Integrated Set of Crystallographic Programs*. In *On the Oxygen Coordination of Cerium in Some Sulfates and Chromates*. Thesis, Department of Inorganic Chemistry, Chalmers Univ. of Technology and Univ. of Göteborg, Göteborg, Sweden.
- LINDQVIST, O. & LJUNGSTRÖM, E. (1979). *J. Appl. Cryst.* **12**, 134.
- MEYER, H.-J. (1963). *Acta Cryst.* **16**, 788–791.
- PETERS, K., VON SCHNERING, H. G., OTT, W. & SEIDENSPINNER, H.-M. (1984). *Acta Cryst.* **C40**, 789–790.