

## The Crystal Structure of the Solid Electrolyte $\text{Ag}_{44}\text{I}_{53}(\text{C}_{11}\text{H}_{30}\text{N}_3)_3$

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(Received 5 July 1977; accepted 8 August 1977)

The crystal structure of  $\text{Ag}_{44}\text{I}_{53}(\text{C}_{11}\text{H}_{30}\text{N}_3)_3$  has been solved by direct methods and refined to  $R = 0.103$ . The crystals are monoclinic ( $C2/c$ ), with cell parameters  $a = 61.40$  (4),  $b = 13.69$  (2),  $c = 22.23$  (2) Å,  $\beta = 108.71$  (5)° and  $Z = 4$ . The structure represents a conducting phase of the solid electrolyte system formed between AgI and  $N,N,N,N',N'',N''$ -heptamethyl- $N'$ -hydrodiethylenetriamine triiodide.

### Introduction

Many double-salt solid electrolytes which contain AgI as one component in high concentration (up to 97 mol % AgI) have anomalously high ionic conductivities at room temperature (Owens, 1973; Coetzer & Thackeray, 1976). In particular, quaternary amine iodide salts react with AgI to form numerous solid electrolyte systems with conductivities reaching  $0.11 \Omega^{-1} \text{cm}^{-1}$  at 20°C (Owens, 1970; Owens, Christie & Tiedeman, 1971; Berardelli, Biondi, De Rossi, Fonseca & Giomini, 1972; Coetzer & Thackeray, 1976). Several crystal structure analyses of the conducting phases of these systems have been undertaken to study their structure–conductivity relations (Geller & Lind, 1970; Geller & Owens, 1972; Geller, Skarstad & Wilber, 1975; Coetzer, Kruger & Thackeray, 1976; Thackeray & Coetzer, 1976*a,b*). It has been established that the electrolytes are characterized by several common structural features.

(1) The  $\text{I}^-$  ions form networks of face-sharing polyhedra (generally tetrahedra) which provide passageways for the mobile  $\text{Ag}^+$  ions.

(2) The structures contain many more  $\text{I}^-$  polyhedra than  $\text{Ag}^+$  ions and the  $\text{Ag}^+$  ions are disordered non-randomly over the crystallographically non-equivalent sets of polyhedral sites.

(3) The  $\text{N}^+$  ions of the amine molecules stabilize the  $\text{I}^-$  lattice and may be regarded as forming part of this lattice, forming polyhedra with neighbouring  $\text{I}^-$  ions.

This paper reports the crystal structure of the solid electrolyte  $\text{Ag}_{44}\text{I}_{53}(\text{C}_{11}\text{H}_{30}\text{N}_3)_3$  which is formed when AgI is reacted with  $N,N,N,N',N'',N''$ -heptamethyl- $N'$ -hydrodiethylenetriamine triiodide ( $\text{C}_{11}\text{H}_{30}\text{N}_3\text{I}_3$ ). From a graph of electrical conductivity *vs* electrolyte composition for the  $\text{AgI}/\text{C}_{11}\text{H}_{30}\text{N}_3\text{I}_3$  electrolyte system (Thackeray & Coetzer, 1978) it was ascertained that the conductivity of this system reaches a maximum of  $0.029 \Omega^{-1} \text{cm}^{-1}$  corresponding to an electrolyte containing 93.5 mol % AgI. The AgI concentration in  $\text{Ag}_{44}\text{I}_{53}(\text{C}_{11}\text{H}_{30}\text{N}_3)_3$  is 93.6 mol % and it seems likely therefore that this structure represents the best conducting phase of the electrolyte system.

### Experimental

A polycrystalline sample of the electrolyte was prepared from a mixture of 94 mol % AgI and 6 mol % of the parent triamine triiodide salt according to a method described by Owens (1970). Finely ground powders of AgI and the triiodide salt were thoroughly mixed with a few drops of  $\text{H}_2\text{O}$  to form a paste. The mixture was dried under vacuum at 80°C, compressed into a pellet at 1 kbar and annealed at 130°C under an  $\text{N}_2$  atmosphere for 60 h. The electrolyte pellet was ground into a fine powder, added to a small quantity of dimethyl sulphoxide and vigorously stirred at 130°C for several hours. The solvent was very slowly removed by controlled vacuum pumping. Small single crystals, generally irregularly shaped and badly faceted, were isolated from the resulting matrix for data collection.

The density of the crystals was determined from the mass and volume of a polycrystalline electrolyte pellet and was found to be in excellent agreement with the density as calculated from crystallographic data. The crystal data are given in Table 1.

Unit-cell dimensions were measured from a least-squares refinement of the angular settings of 25 high-order reflections. Intensities were collected at room temperature from a  $0.08 \times 0.12 \times 0.16$  mm crystal on a Philips PW1100 diffractometer with graphite-monochromated  $\text{Mo } K\alpha$  radiation ( $\lambda = 0.7107$  Å). 5574 reflections were collected over the range  $3 \leq \theta \leq 20^\circ$  in the  $\omega$ - $2\theta$  mode (scan rate =  $0.03^\circ \theta \text{ s}^{-1}$ , scan width =  $0.7^\circ \theta$ ). Background was counted for half the scan time on each side of a reflection. 2257 reflections were considered to be unobserved according to the criterion

Table 1. *Crystal data*

Formula	$\text{Ag}_{44}\text{I}_{53}(\text{C}_{11}\text{H}_{30}\text{N}_3)_3$	$\beta$	108.71 (5)°
Formula weight	12086.1	$Z$	4
Space group	$C2/c$	$D_c$	4.54 g cm <sup>-3</sup>
$a$	61.40 (4) Å	$D_m$	4.57
$b$	13.69 (2)	$\mu$	139.88 cm <sup>-1</sup>
$c$	22.23 (2)		

$I_{\text{rel}} < 1.65\sigma(I_{\text{rel}})$ , where  $\sigma(I_{\text{rel}}) = [(0.02S)^2 + S + B]^{1/2}$ ,  $S$  = scan count and  $B$  = background count. Three standard reflections measured every 3 h were stable to 4.2% from their mean values. Intensities were corrected for Lorentz and polarization effects but not for absorption.

### Structure determination and refinement

Systematic absences,  $h + k = 2n + 1$  for the  $hkl$  and  $l = 2n + 1$  for the  $h0l$  reflections, indicated the two possible space groups  $Cc$  (noncentrosymmetric) or  $C2/c$  (centrosymmetric). The structure was solved by direct methods with the multiple-solution technique incorporated in the program *MULTAN* 74 (Declercq, Germain, Main & Woolfson, 1973). With the structure assumed to be centrosymmetric ( $C2/c$ ), two origin-defining and five additional reflections were selected, from which the phases of 250 reflections with  $E > 2.11$  were generated. Computations of  $E$  maps and all other crystallographic calculations were carried out with *XRAY* 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The phase set with the highest 'combined figure of merit' yielded an  $E$  map from which the positions of the I ions were obtained. These ions formed a three-dimensional network of face-sharing polyhedra (tetrahedra and square pyramids). The remainder of the structure was located from successive

difference maps. The  $\text{Ag}^+$  ions were located within the I polyhedra but were extensively disordered throughout the structure. Only the  $\text{N}^+$  ions of the triamine molecules could be satisfactorily located.

On account of the large number of variable atomic parameters (109 atoms contributing to the asymmetric unit) and the relatively low number of observed reflections (3317), anisotropic temperature factors were assigned only to the ordered  $\text{I}^-$  ions. Isotropic thermal parameters were assigned to the disordered  $\text{Ag}^+$  ions. The  $\text{N}^+$  ions were given an isotropic temperature factor equal to the overall value obtained from a Wilson plot, but this was kept constant during refinement of the structure. The population parameters of the  $\text{Ag}^+$  ions were varied independently of the thermal parameters, except during the last two cycles of refinement when all atomic parameters were varied simultaneously. As a result of the high number of variables, refinement of the structure was carried out with a blocked matrix. Unit weights were applied to all reflections. The final  $R$  was 0.103. Scattering factors used were those of Cromer & Mann (1968). Final atomic positional and population parameters are listed in Table 2.\*

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32980 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Positional ( $\times 10^4$ ) and population parameters (p.p.)

Position	p.p.	$x$	$y$	$z$	Position	p.p.	$x$	$y$	$z$		
I(1)	8(f)	1.0	566 (2)	1225 (5)	810 (3)	Ag(1)	8(f)	0.50 (3)	4039 (4)	311 (14)	2378 (8)
I(2)	8(f)	1.0	2490 (1)	1340 (4)	1300 (3)	Ag(2)	8(f)	0.62 (3)	4796 (3)	327 (11)	392 (7)
I(3)	8(f)	1.0	1984 (1)	1345 (4)	2549 (2)	Ag(3)	8(f)	0.51 (3)	4378 (3)	582 (12)	4308 (7)
I(4)	8(f)	1.0	1051 (1)	1369 (5)	4472 (3)	Ag(4)	8(f)	0.58 (3)	2396 (3)	1345 (12)	3760 (7)
I(5)	8(f)	1.0	2847 (1)	1239 (4)	3655 (2)	Ag(5)	8(f)	0.51 (2)	3420 (3)	1339 (12)	2902 (7)
I(6)	8(f)	1.0	3600 (1)	1363 (4)	4231 (2)	Ag(6)	8(f)	0.58 (3)	1143 (3)	701 (12)	3337 (7)
I(7)	8(f)	1.0	4432 (1)	1357 (5)	2297 (3)	Ag(7)	8(f)	0.58 (3)	4718 (3)	634 (13)	1591 (8)
I(8)	8(f)	1.0	1282 (1)	1992 (4)	2514 (3)	Ag(8)	8(f)	0.54 (3)	4676 (3)	1404 (12)	3645 (7)
I(9)	8(f)	1.0	3745 (1)	1958 (4)	2275 (3)	Ag(9)	8(f)	0.41 (3)	3877 (5)	2498 (18)	3653 (11)
I(10)	8(f)	1.0	1801 (1)	2646 (4)	4393 (3)	Ag(10)	8(f)	0.39 (3)	1034 (5)	2576 (19)	3466 (11)
I(11)	8(f)	1.0	576 (1)	2685 (5)	2649 (3)	Ag(11)	8(f)	0.53 (3)	882 (4)	3183 (16)	3880 (10)
I(12)	8(f)	1.0	4364 (1)	2634 (4)	4094 (3)	Ag(12)	8(f)	0.45 (2)	630 (4)	3032 (13)	1437 (8)
I(13)	8(f)	1.0	3118 (1)	2936 (5)	2375 (3)	Ag(13)	8(f)	0.43 (3)	4185 (4)	2798 (15)	2792 (9)
I(14)	8(f)	1.0	2404 (1)	3333 (5)	4208 (3)	Ag(14)	8(f)	0.34 (3)	2894 (6)	2876 (22)	4443 (13)
I(15)	8(f)	1.0	2435 (1)	3826 (5)	2315 (3)	Ag(15)	8(f)	0.42 (3)	3475 (6)	3010 (22)	4900 (14)
I(16)	8(f)	1.0	587 (1)	4385 (5)	4412 (3)	Ag(16)	8(f)	0.25 (3)	1936 (9)	2877 (33)	3278 (20)
I(17)	8(f)	1.0	3151 (1)	4525 (4)	4192 (2)	Ag(17)	8(f)	0.52 (3)	1501 (4)	3556 (15)	3232 (9)
I(18)	8(f)	1.0	242 (1)	4380 (5)	851 (3)	Ag(18)	8(f)	0.25 (3)	2747 (7)	3351 (27)	3559 (16)
I(19)	8(f)	1.0	969 (1)	4453 (4)	1485 (3)	Ag(19)	8(f)	0.24 (4)	2134 (13)	3251 (47)	2998 (29)
I(20)	8(f)	1.0	1774 (1)	4655 (5)	2728 (3)	Ag(20)	8(f)	0.50 (3)	2819 (4)	4489 (14)	1969 (8)
I(21)	8(f)	1.0	1206 (1)	4499 (4)	3796 (3)	Ag(21)	8(f)	0.53 (3)	2249 (3)	4680 (13)	3175 (8)
I(22)	8(f)	1.0	2721 (1)	4676 (5)	662 (3)	Ag(22)	8(f)	0.43 (3)	4184 (5)	4621 (19)	3492 (11)
I(23)	8(f)	1.0	3452 (1)	4548 (4)	1186 (3)	Ag(23)	8(f)	0.45 (3)	3222 (5)	2691 (21)	3729 (13)
I(24)	8(f)	1.0	4241 (1)	4535 (4)	2272 (3)	Ag(24)	8(f)	0.48 (3)	3785 (4)	4022 (15)	2376 (9)
I(25)	8(f)	1.0	3736 (1)	4554 (4)	3580 (2)	Ag(25)	8(f)	0.25 (3)	504 (8)	4502 (31)	3101 (18)
I(26)	8(f)	1.0	4888 (2)	2218 (6)	1051 (4)	Ag(26)	8(f)	0.49 (3)	906 (4)	468 (17)	1797 (9)
I(27)	4(e)	1.0	0	4341 (6)	2500	Ag(27)	8(f)	0.44 (3)	1896 (5)	910 (18)	3783 (11)

Table 2 (cont.)

Position	p.p.	x	y	z	Position	p.p.	x	y	z		
Ag(28)	8(f)	0.30 (3)	1935 (7)	684 (28)	4544 (17)	Ag(56)	8(f)	0.17 (3)	1030 (12)	3383 (50)	4556 (30)
Ag(29)	8(f)	0.29 (3)	3597 (7)	770 (29)	3037 (18)	Ag(57)	8(f)	0.08 (2)	2637 (16)	3354 (53)	1611 (32)
Ag(30)	8(f)	0.41 (2)	2466 (4)	1754 (14)	2542 (9)	Ag(58)	8(f)	0.35 (3)	3536 (5)	3871 (18)	2375 (11)
Ag(31)	8(f)	0.45 (3)	804 (4)	2584 (15)	1708 (9)	Ag(59)	8(f)	0.23 (3)	715 (8)	4488 (31)	3248 (18)
Ag(32)	8(f)	0.33 (3)	420 (6)	4473 (25)	2176 (15)	Ag(60)	8(f)	0.20 (4)	1374 (12)	2706 (51)	4559 (30)
Ag(33)	8(f)	0.45 (3)	3365 (5)	4888 (20)	2409 (12)	Ag(61)	8(f)	0.11 (3)	3947 (15)	1538 (60)	3669 (37)
Ag(34)	8(f)	0.20 (5)	2839 (12)	469 (62)	2351 (23)	Ag(62)	8(f)	0.17 (3)	3099 (11)	4695 (44)	1743 (26)
Ag(35)	8(f)	0.28 (3)	2224 (6)	227 (23)	1909 (14)	Ag(63)	8(f)	0.09 (3)	4404 (23)	895 (94)	3594 (57)
Ag(36)	8(f)	0.36 (3)	4822 (7)	782 (27)	3326 (16)	Ag(64)	8(f)	0.17 (3)	4091 (10)	1127 (39)	4349 (24)
Ag(37)	8(f)	0.33 (4)	822 (8)	1327 (33)	2053 (20)	Ag(65)	8(f)	0.13 (3)	2422 (19)	239 (73)	3310 (45)
Ag(38)	8(f)	0.25 (5)	2897 (9)	1101 (52)	2386 (18)	Ag(66)	8(f)	0.17 (3)	2193 (14)	1573 (57)	3904 (35)
Ag(39)	8(f)	0.11 (3)	2245 (19)	1719 (74)	4630 (45)	Ag(67)	8(f)	0.10 (4)	3573 (25)	3336 (103)	4344 (62)
Ag(40)	8(f)	0.35 (3)	951 (6)	1366 (24)	3093 (14)	Ag(68)	8(f)	0.09 (2)	3168 (14)	1262 (48)	2991 (29)
Ag(41)	8(f)	0.34 (2)	2681 (4)	2003 (15)	2476 (9)	Ag(69)	8(f)	0.08 (3)	2769 (20)	2485 (79)	4733 (48)
Ag(42)	8(f)	0.21 (3)	3595 (11)	2645 (41)	3250 (25)	Ag(70)	8(f)	0.14 (3)	1526 (15)	1215 (60)	4592 (36)
Ag(43)	8(f)	0.26 (2)	3391 (6)	3137 (21)	3673 (13)	Ag(71)	8(f)	0.16 (4)	2419 (16)	893 (68)	2458 (42)
Ag(44)	8(f)	0.30 (3)	4027 (7)	3383 (26)	2960 (16)	Ag(72)	8(f)	0.16 (4)	4022 (17)	1943 (73)	4760 (44)
Ag(45)	8(f)	0.33 (3)	2866 (6)	3850 (26)	4956 (16)	Ag(73)	8(f)	0.14 (3)	1318 (14)	2472 (53)	3802 (32)
Ag(46)	8(f)	0.35 (3)	1328 (5)	4072 (21)	2722 (13)	Ag(74)	8(f)	0.17 (2)	2885 (8)	3251 (29)	3262 (18)
Ag(47)	8(f)	0.34 (3)	2663 (6)	4478 (24)	3571 (14)	Ag(75)	8(f)	0.11 (3)	2926 (19)	4470 (77)	2895 (46)
Ag(48)	8(f)	0.33 (3)	826 (6)	4599 (22)	2628 (13)	Ag(76)	8(f)	0.15 (3)	1280 (13)	4806 (48)	2613 (29)
Ag(49)	8(f)	0.33 (4)	2750 (8)	4741 (32)	4442 (20)	Ag(77)	4(e)	0.18 (4)	0	6378 (46)	2500
Ag(50)	8(f)	0.21 (3)	129 (11)	5257 (45)	3734 (27)	N(1)	8(f)	1.0	3053 (13)	1294 (46)	228 (28)
Ag(51)	8(f)	0.16 (3)	4153 (13)	1202 (51)	3061 (31)	N(2)	8(f)	1.0	3456 (13)	2125 (46)	-549 (28)
Ag(52)	8(f)	0.20 (3)	1425 (9)	1426 (36)	3935 (22)	N(3)	8(f)	1.0	3960 (12)	2651 (47)	244 (28)
Ag(53)	8(f)	0.18 (3)	1716 (10)	1258 (36)	3366 (22)	N(4)	4(e)	1.0	0	-33 (66)	2500
Ag(54)	8(f)	0.23 (3)	2502 (9)	1427 (35)	4272 (21)	N(5)	8(f)	1.0	177 (13)	1073 (46)	3969 (28)
Ag(55)	8(f)	0.28 (4)	3921 (8)	2808 (33)	4235 (20)						

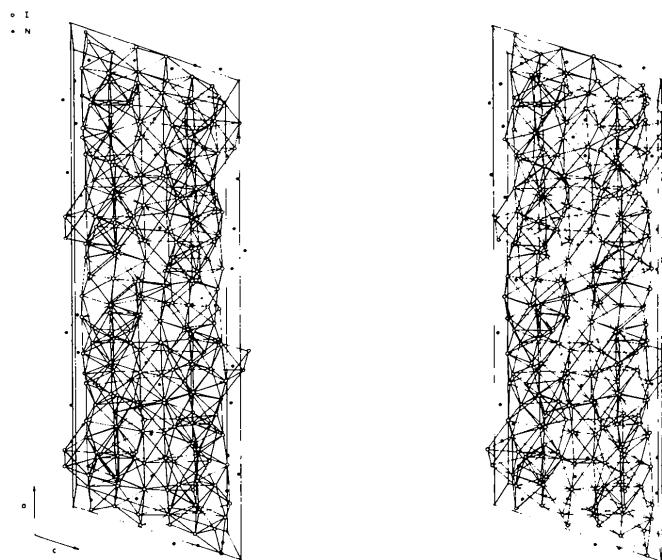


Fig. 1. A stereoscopic illustration of the unit cell of  $\text{Ag}_{44}\text{I}_{33}(\text{C}_{11}\text{H}_{30}\text{N}_3)_3$ .  $\text{Ag}^+$  ions have been omitted for clarity.  $\text{I}^-$  ions are joined by solid lines. The dotted lines indicate the separation between  $\text{N}^+$  ions in the triamine molecules.

### Discussion

A stereoscopic illustration of the structure of  $\text{Ag}_{44}\text{I}_{33}^-(\text{C}_{11}\text{H}_{30}\text{N}_3)_3$  is given in Fig. 1 (Johnson, 1965). Although the structure is highly complex, the features

are essentially the same as those found in other quaternary amine iodide/ $\text{AgI}$  solid electrolytes (Geller & Lind, 1970; Geller & Owens, 1972; Geller, Skarstad & Wilber, 1975; Coetzer, Kruger & Thackeray, 1976; Thackeray & Coetzer, 1976a,b). The  $\text{I}^-$  ions, which are

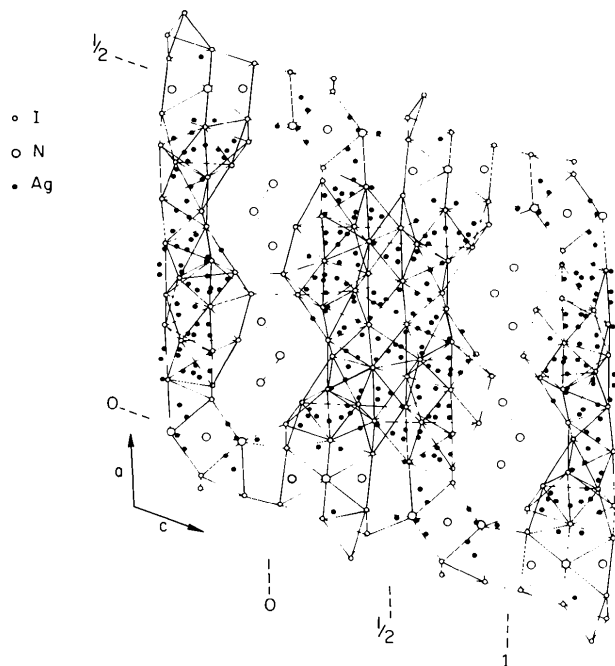


Fig. 2. A [010] projection down  $b/2$ .

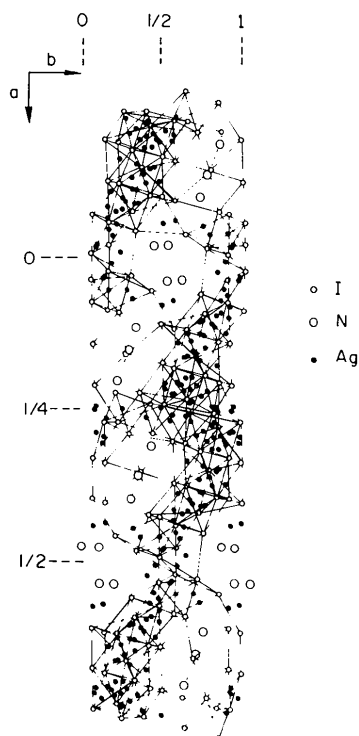


Fig. 3. A [001] projection down  $c/2$ .

joined by solid lines, form a three-dimensional lattice of face-sharing polyhedra. The polyhedra are of two basic types, irregular tetrahedra and square pyramids. The polyhedra are interlinked to form continuous passageways along which the  $\text{Ag}^+$  ions are able to diffuse.  $\text{Ag}^+$  ions are located within the polyhedra but are disordered throughout the structure. They have been omitted from the figure for clarity. In the conduction mechanism the  $\text{Ag}^+$  ions pass through the faces of the  $\text{I}^-$  polyhedra from one polyhedral site to another. The triamine molecules reside in holes in the  $\text{I}^-$  lattice.  $\text{N}^+ \cdots \text{N}^+$  separations in each triamine chain are indicated by dotted lines.

The three-dimensional character of the electrolyte is shown in Figs. 2 and 3. In each figure the projection is down half a unit-cell axis. Fig. 2 is a [010] projection of the structure and shows the wide distribution of disordered  $\text{Ag}^+$  ions in face-sharing  $\text{I}^-$  polyhedra in the  $ac$  plane. The holes in the  $\text{I}^-$  lattice which contain the triamine molecules are clearly visible. Fig. 3 represents the structure when viewed down  $c$  and indicates the direction of movement of the  $\text{Ag}^+$  ions in channels of face-sharing  $\text{I}^-$  polyhedra in the  $a$  and  $b$  directions. It is evident that conduction through the structure is anisotropic.

There are 84  $\text{I}^-$  tetrahedra in the asymmetric unit, 76 of which contain disordered  $\text{Ag}^+$  ions. All these  $\text{Ag}^+$  ions reside in 8( $f$ ) general positions. The  $\text{I}^-$ - $\text{I}^-$  tetrahedral distances are all  $< 5.5 \text{ \AA}$ , the average distance being  $4.63 \text{ \AA}$ . In addition to the  $\text{I}^-$  tetrahedra, the asymmetric unit contains three irregularly shaped square pyramids, the  $\text{I}^-$ - $\text{I}^-$  diagonal distances at the base of each pyramid being  $> 6.0 \text{ \AA}$ . Each  $\text{I}^-$  pyramid combines with an  $\text{N}^+$  ion of a triamine molecule to form an irregular octahedron. One of the pyramids [1(7), 1(7'), 1(26), 1(26'), 1(27) in Fig. 4] contains a disordered  $\text{Ag}^+$  ion [Ag(77)]. This ion is located in a special position [4( $e$ )] at  $(\frac{1}{2}, 0.1378, \frac{1}{4})$ , and has an occupancy of 0.18. The other two pyramids are empty. The  $\text{I}^-$  pyramids share their triangular faces with adjacent tetrahedra and consequently contribute to the conduction pathways of the  $\text{Ag}^+$  ions. Taking into consideration the 672  $\text{I}^-$  tetrahedra and 20  $\text{I}^-$  pyramids in the unit cell, there are 692 possible sites for the 176  $\text{Ag}^+$  ions.

The formula unit of the electrolyte, derived from the 53  $\text{I}^-$  ions and the three triamine molecules in one quarter of the unit cell is  $\text{Ag}_{44}\text{I}_{53}(\text{C}_{11}\text{H}_{30}\text{N}_3)_3$ . The distribution of the  $\text{Ag}^+$  ions over the crystallographically non-equivalent sets of sites is markedly non-random, with population parameters of these ions varying between 0.08 (3) and 0.62 (3). The sum of these parameters for the 153 disordered  $\text{Ag}^+$  ions in one quarter of the unit cell is 47.28 as opposed to the 44.00 required by stoichiometry. This represents an overall error of 7.5% in the population parameters. The thermal parameters\* of the  $\text{Ag}^+$  ions are large, as

\* See deposition footnote on p. 72.

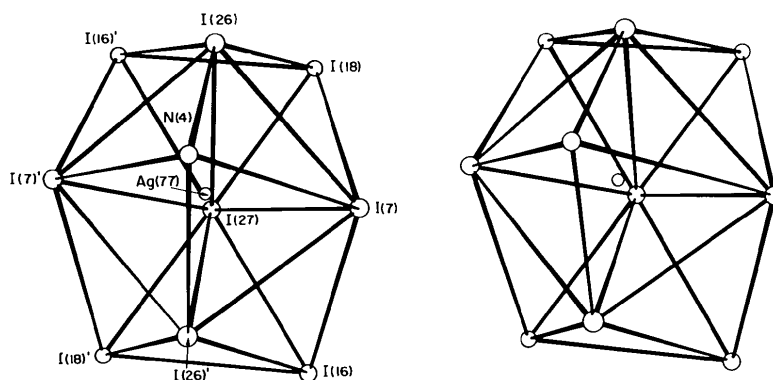


Fig. 4. A stereoscopic illustration of the  $I^-$  pyramid  $[I(7), I(7)', I(26), I(26)', I(27)]$  containing  $Ag(77)$ . The pyramid combines with  $N(4)$  to form an octahedron, and shares its  $I^-$  triangular faces with neighbouring tetrahedra [e.g.  $I(7)', I(16)', I(26), I(27)$ ].

Table 3. *Interatomic distances* (Å)

	Minimum	Maximum	Mean
$I^- - I^-$ (tetrahedral and square pyramidal)	3.96 (1)	5.48 (1)	4.63
$Ag^+ - I^-$ (a) in tetrahedra	2.38 (10)	3.28 (9)	2.87
(b) in square pyramid	2.79 (6)	3.37 (1)	3.22
$Ag^+ - Ag^+$ (a) in adjacent face-shared tetrahedra	0.93 (11)	2.73 (13)	1.80
(b) in adjacent face-shared tetrahedra and square pyramids	2.42 (3)	2.55 (5)	2.49
$N^+ - I^-$	4.55 (8)	5.58 (8)	5.06

expected, and are indicative of the high mobility of these ions at room temperature. The distances between  $Ag^+$  ions in adjacent face-shared polyhedra are very short and vary between 0.93 (11) and 2.73 (13) Å. It is evident that these polyhedra cannot be occupied simultaneously, the  $Ag-Ag$  distance in metallic silver being 2.90 Å (Sutton, 1965).

There are two crystallographically non-equivalent triamine molecules in the unit cell. One lies in a general position while the second is disordered about a twofold axis, for example at  $(0, y, \frac{1}{4})$ . The  $N^+$  ions of the triamine chains,  $N(1), N(2), N(3), N(4)$  and  $N(5)$  are surrounded by 13, 9, 11, 6 and 11  $I^-$  neighbours, respectively, with  $N^+ - I^-$  distances varying between 4.55 (8) and 5.58 (8) Å.

Because of the very large number of independent nearest neighbour  $I^- - I^-$ ,  $Ag^+ - Ag^+$ ,  $Ag^+ - I^-$  and  $N^+ - I^-$  distances in the asymmetric unit, only maximum, minimum and mean values have been tabulated (Table 3). The values are consistent with those reported

for the electrolyte structures of  $Ag_{11}I_{13}C_9H_{24}N_2$ , and  $Ag_{21}I_{25}(C_9H_{24}N_2)_2$  (Thackeray & Coetzer, 1976a,b).

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