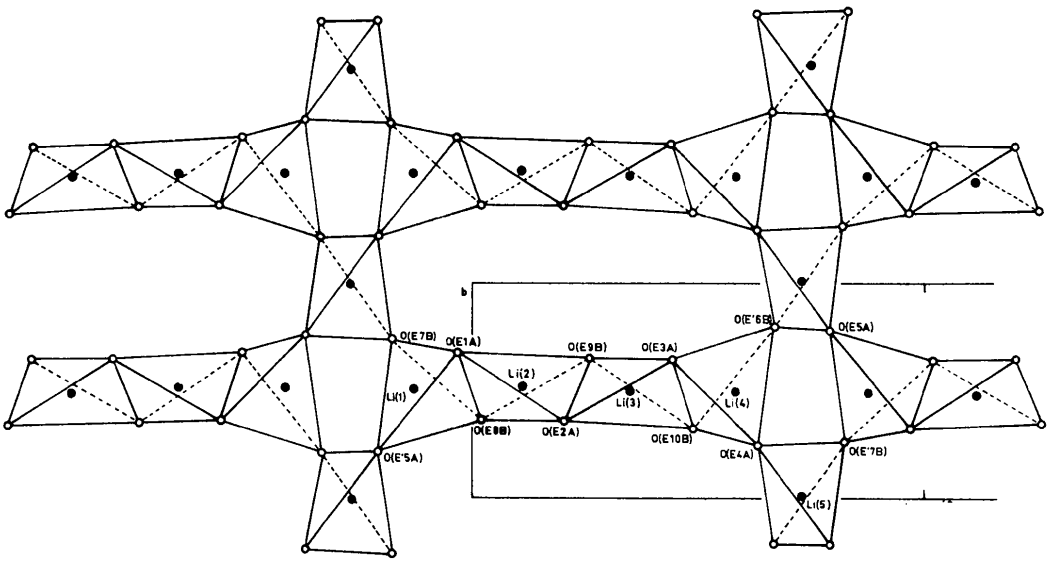

Fig. 2. Projection suivant la direction [101] de l'enchaînement des cations associés dans $LiPO_3$. L'axe horizontal est $(a-c)/2$.

La Fig. 2 représente l'enchaînement des cations associés projeté sur un plan $\mathbf{b},(\mathbf{a}-\mathbf{c})/2$. Tous les atomes de Li se trouvent dans des tétraèdres d'oxygène qui s'enchaînent soit par des arêtes soit par des sommets pour former un réseau bidimensionnel. Les atomes d'oxygène qui composent les tétraèdres LiO_4 sont tous des atomes d'oxygène extérieurs de la chaîne $(PO_3)_\infty$.

Il s'agit du deuxième exemple de chaîne de période dix tétraèdres. Le premier exemple était fourni par le polyphosphate de baryum potassium: $Ba_2K(PO_3)_5$ (Martin, Tordjman & Durif, 1975).

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The Crystal Structure of the Solid Electrolyte: Silver Iodide–*N*,*N*,*N*,*N*′,*N*′,*N*′-Hexamethyl-1,3-propylenediamine Diiodide(I)

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The structure of the solid electrolyte $Ag_{21}I_{25}(C_9H_{24}N_2)_2$ has been solved by direct methods and refined to $R=0{\cdot}122$ with 2567 independent reflexions. The crystals are monoclinic ($C2/c$) with $a=22{\cdot}46$ (2), $b=12{\cdot}97$ (2), $c=30{\cdot}59$ (2) Å, $\beta=104{\cdot}15$ (5)°, $Z=4$. Intensities were collected on a four-circle diffractometer with Mo $K\alpha$ radiation. The structure consists of a three-dimensional I lattice which contains conduction pathways for the Ag^+ ions. The I lattice is interrupted to contain the diamine chains.

Introduction

Numerous solid electrolytes with ionic conductivities of up to 0·11 $\Omega^{-1}\,cm^{-1}$ have been synthesized by reacting AgI with various quaternary amine iodides (Owens, 1970; Owens Christie & Tiedeman 1971; Coetzer & Thackeray, 1976). Structural studies of several conducting phases have been undertaken to investigate the structure–conductivity relationships of these electrolyte systems (Geller & Lind, 1970; Geller & Owens, 1972; Geller, Skarstad & Wilber, 1975; Coetzer, Kruger & Thackeray, 1976). The structures consist of face-sharing I tetrahedra and octahedra which provide a network of passageways along which the Ag^+ ions are able to diffuse. Ag^+ ions are located in tetrahedral and octahedral sites and as there are generally three to four

sites for each Ag^+ ion, these ions can move rapidly through the polyhedral faces from one site to another. As a result of this diffusion the Ag^+ ions are extensively disordered throughout the I lattice. $Ag_{21}I_{25}(C_9H_{24}N_2)_2$ is one of the conducting phases that has been isolated from the AgI/*N*,*N*,*N*,*N*′,*N*′,*N*′-hexamethyl-1,3-prop-

Table 1. *Positional* ($\times 10^4$) *and thermal* ($\times 10^3$) *parameters*

Standard deviations are given in parentheses. Anisotropic temperature factors are of the form:

$$T=\exp[-2\pi(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)].$$

	Position	Population parameter	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	4(*d*)	1·0 (0)	2500 (0)	2500 (0)	5000 (0)	54 (5)	53 (5)	68 (5)	−1 (5)	17 (4)	2 (5)
I(2)	4(*e*)	1·0 (0)	0 (0)	824 (7)	2500 (0)	39 (5)	50 (6)	113 (8)	0 (0)	−8 (5)	0 (0)
I(3)	4(*e*)	1·0 (0)	5000 (0)	2502 (7)	2500 (0)	42 (4)	35 (4)	103 (6)	0 (0)	29 (4)	0 (0)
I(4)	8(*f*)	1·0 (0)	3340 (3)	836 (5)	2506 (3)	67 (4)	47 (4)	145 (6)	10 (4)	59 (4)	29 (4)
I(5)	8(*f*)	1·0 (0)	3649 (3)	4300 (5)	3220 (2)	71 (4)	63 (4)	42 (3)	−5 (3)	18 (3)	2 (3)
I(6)	8(*f*)	1·0 (0)	137 (3)	4219 (5)	3225 (2)	69 (4)	58 (4)	55 (4)	4 (3)	18 (3)	−5 (3)
I(7)	8(*f*)	1·0 (0)	3069 (3)	3988 (5)	1781 (2)	56 (4)	75 (5)	45 (3)	−5 (3)	5 (3)	−5 (3)
I(8)	8(*f*)	1·0 (0)	1688 (2)	2501 (5)	2564 (2)	41 (3)	37 (3)	73 (4)	2 (3)	17 (3)	3 (3)
I(9)	8(*f*)	1·0 (0)	687 (2)	4223 (5)	4741 (2)	54 (4)	44 (4)	67 (4)	−3 (3)	20 (3)	3 (3)
I(10)	8(*f*)	1·0 (0)	2583 (2)	4053 (4)	259 (2)	45 (3)	51 (4)	56 (3)	3 (3)	13 (3)	−1 (3)
I(11)	8(*f*)	1·0 (0)	4133 (3)	4229 (5)	4738 (2)	53 (3)	44 (4)	61 (4)	5 (3)	14 (3)	1 (3)
I(12)	8(*f*)	1·0 (0)	3204 (3)	1415 (5)	3846 (2)	69 (4)	58 (4)	73 (4)	9 (3)	20 (3)	3 (3)
I(13)	8(*f*)	1·0 (0)	1031 (3)	1409 (5)	3844 (2)	73 (4)	57 (4)	77 (4)	−4 (3)	22 (3)	−3 (3)
I(14)	8(*f*)	1·0 (0)	2112 (3)	4671 (5)	3850 (2)	62 (4)	65 (4)	80 (4)	1 (4)	22 (3)	1 (3)
Ag(1)	8(*f*)	0·31 (5)	3008 (18)	2821 (34)	2589 (21)	135 (34)	125 (38)	95 (45)	15 (24)	33 (23)	45 (27)
Ag(2)	8(*f*)	0·47 (3)	3761 (9)	2846 (15)	2529 (8)	84 (16)	67 (15)	145 (20)	15 (10)	25 (13)	−13 (12)
Ag(3)	8(*f*)	0·42 (3)	2510 (12)	4278 (25)	2535 (11)	90 (18)	116 (26)	172 (30)	25 (17)	46 (17)	−11 (21)
Ag(4)	8(*f*)	0·42 (3)	2156 (11)	325 (23)	2554 (10)	79 (18)	105 (25)	158 (27)	−40 (16)	18 (16)	7 (17)
Ag(5)	8(*f*)	0·42 (3)	4553 (9)	464 (14)	2484 (7)	88 (16)	51 (14)	104 (18)	−17 (11)	28 (12)	6 (11)
Ag(6)	8(*f*)	0·29 (3)	906 (15)	4246 (25)	2604 (14)	106 (26)	71 (23)	214 (40)	50 (20)	101 (25)	43 (23)
Ag(7)	8(*f*)	0·32 (4)	1251 (17)	428 (23)	2610 (18)	159 (36)	64 (22)	134 (43)	−57 (21)	81 (26)	−21 (20)
Ag(8)	8(*f*)	0·41 (3)	368 (13)	2849 (15)	2535 (10)	174 (27)	39 (14)	158 (27)	−12 (12)	83 (24)	−26 (14)
Ag(9)	8(*f*)	0·37 (3)	2013 (11)	2485 (23)	3548 (9)	98 (21)	106 (22)	110 (22)	11 (18)	36 (15)	0 (18)
Ag(10)	8(*f*)	0·25 (4)	3020 (16)	2492 (38)	2973 (23)	102 (28)	98 (32)	82 (54)	−12 (25)	9 (22)	−51 (32)
Ag(11)	8(*f*)	0·24 (4)	1209 (18)	687 (39)	2967 (20)	76 (29)	118 (36)	81 (43)	24 (24)	8 (21)	31 (29)
Ag(12)	8(*f*)	0·50 (2)	2165 (7)	399 (13)	3985 (6)	62 (11)	79 (12)	116 (16)	−16 (10)	32 (10)	−10 (11)
Ag(13)	8(*f*)	0·31 (3)	1910 (11)	4500 (22)	4718 (8)	67 (20)	85 (23)	60 (17)	−14 (15)	0 (12)	21 (14)
Ag(14)	8(*f*)	0·33 (3)	2876 (13)	4478 (20)	4711 (10)	101 (23)	63 (19)	111 (24)	11 (15)	41 (17)	9 (15)
Ag(15)	8(*f*)	0·28 (3)	3158 (12)	787 (25)	4727 (12)	47 (18)	69 (23)	152 (32)	11 (15)	13 (16)	13 (20)
Ag(16)	8(*f*)	0·46 (3)	4183 (8)	4183 (16)	2453 (7)	61 (12)	86 (15)	127 (19)	1 (10)	31 (10)	13 (13)
Ag(17)	8(*f*)	0·41 (2)	1079 (8)	3544 (15)	3985 (6)	52 (12)	69 (14)	89 (16)	21 (10)	21 (10)	12 (11)
Ag(18)	8(*f*)	0·21 (3)	1282 (25)	3164 (52)	3388 (24)	102 (45)	151 (61)	227 (69)	−26 (38)	26 (39)	−58 (49)
Ag(19)	8(*f*)	0·28 (3)	1170 (12)	2251 (21)	4722 (10)	69 (19)	66 (22)	102 (26)	−13 (14)	32 (16)	−23 (17)
Ag(20)	8(*f*)	0·29 (2)	3641 (11)	2241 (21)	4728 (9)	52 (18)	67 (22)	84 (23)	−3 (13)	14 (14)	6 (15)
Ag(21)	8(*f*)	0·42 (9)	3222 (14)	3565 (20)	3974 (17)	89 (21)	45 (15)	67 (22)	−1 (11)	34 (17)	−2 (12)
Ag(22)	8(*f*)	0·32 (3)	1634 (12)	769 (21)	4708 (8)	113 (23)	73 (20)	75 (20)	0 (16)	48 (16)	10 (14)
Ag(23)	8(*f*)	0·32 (3)	1366 (16)	3449 (30)	4196 (16)	112 (28)	96 (32)	211 (50)	14 (21)	63 (27)	53 (30)
Ag(24)	8(*f*)	0·27 (5)	2592 (39)	3230 (47)	3313 (24)	383 (119)	128 (56)	257 (81)	51 (59)	197 (81)	13 (47)
Ag(25)	8(*f*)	0·28 (3)	1269 (24)	4256 (47)	3022 (17)	144 (52)	230 (58)	153 (44)	59 (42)	89 (38)	85 (39)
Ag(26)	8(*f*)	0·27 (10)	3120 (25)	3395 (48)	4247 (49)	49 (25)	97 (30)	112 (88)	−13 (19)	−15 (30)	15 (39)
Ag(27)	8(*f*)	0·18 (3)	2429 (21)	788 (46)	2926 (16)	88 (36)	92 (52)	114 (40)	37 (34)	24 (26)	20 (33)
Ag(28)	8(*f*)	0·20 (3)	640 (23)	2427 (54)	2990 (23)	106 (42)	143 (66)	214 (75)	6 (40)	32 (40)	−118 (59)
Ag(29)	8(*f*)	0·19 (2)	2273 (20)	820 (31)	4283 (12)	124 (39)	49 (29)	57 (25)	0 (25)	52 (23)	−1 (19)
Ag(30)	8(*f*)	0·17 (3)	1938 (24)	1133 (39)	3347 (23)	85 (41)	53 (36)	179 (70)	−15 (28)	27 (37)	−8 (35)
Ag(31)	8(*f*)	0·10 (2)	2382 (24)	4319 (41)	2993 (16)	51 (41)	18 (36)	41 (37)	19 (29)	8 (26)	−13 (26)

	Position	Population parameter	x	y	z	Isotropic U (Å^2)
N(1)	8(*f*)	1·0 (0)	4459 (29)	2482 (58)	849 (21)	57
N(2)	8(*f*)	1·0 (0)	1117 (29)	2472 (58)	848 (21)	57
C(1)	8(*f*)	1·0 (0)	5080 (38)	2027 (67)	1019 (27)	57
C(2)†	8(*f*)	1·0 (0)	4500 (–)	3600 (–)	1000 (–)	57
C(3)	8(*f*)	1·0 (0)	4004 (38)	1864 (68)	1016 (27)	57
C(4)†	8(*f*)	1·0 (0)	4100 (–)	2000 (–)	400 (–)	57
C(5)	8(*f*)	1·0 (0)	769 (38)	2575 (76)	0 (28)	57
C(6)†	8(*f*)	1·0 (0)	1100 (–)	2900 (–)	400 (–)	57
C(7)	8(*f*)	1·0 (0)	534 (38)	1927 (69)	979 (28)	57
C(8)†	8(*f*)	1·0 (0)	1200 (–)	3200 (–)	1200 (–)	57
C(9)	8(*f*)	1·0 (0)	1716 (38)	1765 (67)	1008 (27)	57

† Parameters of these atoms were not refined.

ylenediamine diiodide system. The AgI concentration of this compound is 91·3 mol %.

Experimental

92 mol % AgI and 8 mol % *N,N,N,N′,N′,N′*-hexamethyl-1,3-propylenediamine diiodide were thoroughly mixed in a few drops of water, vacuum dried, compressed to 1 kbar, and annealed at 140°C. The reaction mixture was ground and added to a small quantity of DMF and thoroughly stirred at 120°C. The DMF was slowly removed by controlled vacuum pumping over several hours. Small hexagonally shaped, plate-like crystals were isolated from the resulting matrix. We were able to isolate a $0{\cdot}05\times0{\cdot}08\times0{\cdot}10$ mm crystal suitable for data collection.

Crystal data

$a=22{\cdot}46$ (2), $b=12{\cdot}97$ (2), $c=30{\cdot}59$ (2) Å, $\beta=104{\cdot}15$ (5)°, $D_c=4{\cdot}43$ g cm^{-3}, $Z=4$, $\mu=135{\cdot}7$ cm^{-1}; formula weight 5759; formula $Ag_{21}I_{25}(C_9H_{24}N_2)_2$; space group $C2/c$.

The lattice constants were determined from the least-squares refinement of the angular settings of 25 high-order reflexions. Systematic absences $h+k=2n+1$ for the hkl and $l=2n+1$ for the $h0l$ reflexions indicated the two possible space groups Cc and $C2/c$. Intensities were collected on a Philips PW 1100 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å, ω–2θ scan, scan speed $0{\cdot}02°\ \theta\ s^{-1}$, scan width $0{\cdot}7°\ \theta$). 5296 independent reflexions were measured in the range $3\le\theta\le22°$, of which 2729 were considered to be unobserved according to the criterion $I<3{\cdot}0\,\sigma(I)$, where $\sigma(I)=[(0{\cdot}02S)^2+S+B]^{1/2}$, S=scan count and B=background count. The background was counted for half the scan time on each side of a reflexion. The unobserved reflexions were not used during the refinement.

Three reflexions were measured periodically throughout the data collection and showed the crystal to be stable to X-radiation. Lorentz and polarization factors were applied, but no absorption corrections were made.

Solution of the structure

The structure was solved by direct methods with *MULTAN* 74 (Declercq, Germain, Main & Woolfson, 1973). All further computations were carried out with X-RAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

The structure was initially assumed to be centrosymmetric ($C2/c$), based on the distribution of the E values. This was verified by the final structural results. An E map computed from the phases of 250 reflexions with $E>1{\cdot}3$ revealed the positions of the 14 I^- ions. The disordered Ag^+ ions were located from successive difference maps. Full-matrix least-squares isotropic refinement of the heavy atoms yielded an R of 0·187. Anisotropic refinement of these atoms, which necessitated the use of a blocked matrix containing five blocks, reduced R to 0·129. No restraints were put on the population parameters of the Ag^+ ions. Only the two N, the central C and four methyl C atoms of the diamine chain could be satisfactorily located. Weak peaks on the difference map gave an indication of the positions of the remaining light atoms [C(2), C(4), C(6) and C(8)]. The parameters of these four atoms were kept constant during the remainder of the refinement. Each light atom was assigned the isotropic temperature factor equal to the value obtained from a Wilson plot. The final R with unit weight was 0·122 where $R=\sum||F_o|-|F_c||/\sum|F_o|$.

Scattering factors were those of Cromer & Mann (1968). Atomic parameters are listed in Table 1. Interatomic distances are summarized in Table 2. A com-

Table 2. *Interatomic distances* (Å)

	Maximum	Minimum	Mean
I—I	4·98 (1)	4·25 (1)	4·61
Ag–I	3·31 (4)	2·63 (7)	2·85
N—I	5·40 (7)	4·55 (8)	5·07
Ag–Ag	2·60 (8)	0·80 (4)	1·87
N—N	5·04 (9)	–	–

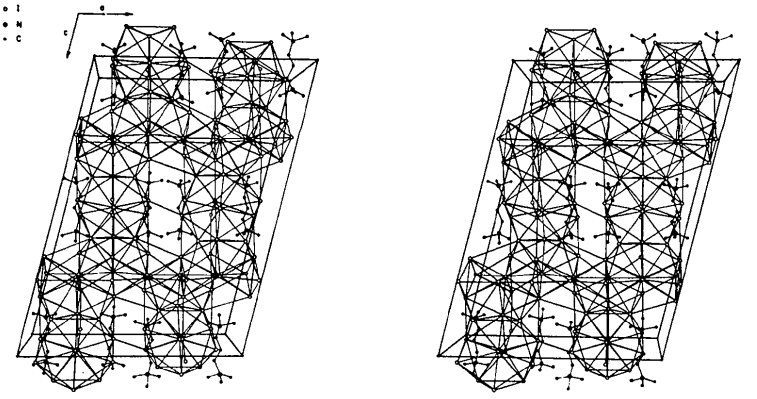

Fig. 1. A [010] stereoscopic projection of the structure showing the I lattice and diamine chains of the unit cell. Ag^+ ions are located in I tetrahedra but have been omitted for clarity.

parison of observed and calculated structure factors is available.†

Discussion

A stereoscopic illustration (Fig. 1, Johnson, 1965) shows the contents of the unit cell. I^- ions are located at the apices of face-sharing tetrahedra. The Ag^+ ions are located in tetrahedral sites but have been omitted from the figure for clarity. The I tetrahedra are interconnected to form several channels along which the Ag^+ ions are able to diffuse. The main channels run parallel to **c*** between the *xy* planes at $z=\frac{1}{4}$ and $\frac{3}{4}$. These channels are separated by the diamine chains but link up as a result of the twofold screw axes located at $x=\frac{1}{4}$ ($\frac{3}{4}$), and $z=\frac{1}{4}$ ($\frac{3}{4}$), and the twofold axes at $x=\frac{1}{2}$ (0) and $z=\frac{1}{4}$ ($\frac{3}{4}$) to provide a continuous zigzag path for the Ag^+ ions along **c***. Channels of face-sharing I tetrahedra also exist within the *xy* planes at $z=\frac{1}{4}$ and $\frac{3}{4}$ which permit the diffusion of Ag^+ ions in the **a** and **b** directions.

There are 84 Ag^+ ions and 256 tetrahedral sites in the unit cell. The Ag^+ ions are distributed over 248 of these sites with population parameters varying from 0·10 (2) to 0·50 (2). The sum of the population parameters of the Ag^+ ions at the end of the refinement for one quarter of the unit cell was 19·42 compared with the value of 21·00 implied by the formula $Ag_{21}I_{25}(C_9H_{24}N_2)_2$.

As there are over 200 nearest-neighbour distances between the Ag^+, I^- and N^+ ions in the asymmetric unit, only maximum, minimum and mean values have been reported (Table 2). I–I tetrahedral distances vary between 4·98 (1) and 4·25 (1) Å. The mean is 4·61 Å. Very short distances exist between Ag^+ ions in adjacent face-shared tetrahedra. They range from 0·80 (4) to 2·60 (8) Å, the mean being 1·87 Å. As the Ag–Ag distance in metallic Ag is 2·89 Å (Sutton, 1965), it is evident that these tetrahedra cannot be occupied simultaneously.

The amine chains lie parallel to **c***. Each N atom has 13 I^- ion neighbours with N–I distances varying between 4·55 (8) and 5·40 (7) Å. These values are consistent with the N–I distances found in the related electrolyte structure $Ag_{11}I_{13}C_9H_{24}N_2$ (Thackeray & Coetzer, 1976).

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31876 (24 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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