JONES, D. W. & SOWDEN, J. M. (1975). *Acta Cryst.* **A31**, S126.
LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932–939.
MULLIKEN, R. S. (1952). *J. Amer. Chem. Soc.* **74**, 811–824.
PAWLEY, G. S. (1971). *Acta Cryst.* **A27**, 80–81.
RIETVELD, H. M., MASLEN, E. N. & CLEWS, C. J. B. (1970). *Acta Cryst.* **B26**, 693–706.
ROBERTSON, G. B. (1961). *Nature, Lond.* **191**, 593.
SHULL, C. G. (1972). Private communication.
THIESSEN, W. E. & BUSING, W. R. (1974). *Acta Cryst.* **A30**, 814–821.
TROTTER, J. (1961). *Acta Cryst.* **14**, 1135–1140.
WILLIAMS, R. M. & WALLWORK, S. C. (1968). *Acta Cryst.* **B24**, 168–174.
YAKUSHI, K., IKEMOTO, I. & KURODA, H. (1974). *Acta Cryst.* **B30**, 835–837.
ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

Acta Cryst. (1976). B**32**, 2197

The Crystal Structure of *N,N,N,N′,N′,N′*-Hexamethylisopropylenediamine Diiodide–Silver Iodide(I)

BY M. M. THACKERAY AND J. COETZER

National Physical Research Laboratory, CSIR, P.O. Box 395, *Pretoria* 0001, *South Africa*

(*Received* 11 *November* 1975; *accepted* 23 *January* 1976)

Crystals of $Ag_{11}I_{13}C_9H_{24}N_2$ are orthorhombic, space group *Ibam*, with $a=13{\cdot}84$ (2), $b=15{\cdot}65$ (2), $c=20{\cdot}69$ (2) Å, $D_c=4{\cdot}44$ g cm^{-3} for $Z=4$. The structure was solved by direct methods with 1084 independent reflexions and refined to $R=0{\cdot}080$. A three-dimensional lattice of face-sharing I tetrahedra permits the conduction of Ag^+ ions through the structure. The Ag^+ ions are situated in the I tetrahedral sites and are extensively disordered. Holes in the I lattice contain the amine chains which are disordered about three mutually perpendicular diad axes.

Introduction

Several quaternary amine iodide salts, when reacted with silver iodide, have been found to produce solid electrolytes with high electrical conductivities. Owens (1970) has studied the tetraalkylammonium iodide–silver iodide system. In particular tetramethylammonium iodide–silver iodide shows a maximum conductivity of 0·04 (Ω cm)$^{-1}$ corresponding to a phase containing approximately 87 mol % AgI and 13 mol % $(CH_3)_4NI$. Geller & Lind (1970) have reported the crystal structure of this phase which has the formula $[(CH_3)_4N]_2Ag_{13}I_{15}$. The results of conductivity measurements made on the hexamethylethylenediamine diiodide–silver iodide and hexamethylisopropylenediamine diiodide–silver iodide systems have recently been reported (Coetzer & Thackeray, 1976*a*). The former system shows a maximum conductivity of 0·11 (Ω cm)$^{-1}$ corresponding to an electrolyte in which the AgI concentration is 97 mol %. We have been able to isolate three phases of this system with AgI concentrations of 67, 86 and 89 mol %, respectively. The structures of these phases have been reported (Coetzer & Thackeray, 1975*a*, *b*; Coetzer, Kruger & Thackeray, 1976). The structure reported here is the first phase to be isolated from the hexamethylisopropylenediamine diiodide–silver iodide system.

Experimental

Irregularly shaped crystals were obtained from a reaction mixture of 93 mol % AgI and 7 mol % hexamethylisopropylenediamine diiodide. The preparation of the reaction mixture is described elsewhere (Coetzer & Thackeray, 1976*b*). A 0·08 × 0·10 × 0·10 mm crystal was selected for data collection. The cell data are: $a=13{\cdot}84$ (2), $b=15{\cdot}65$ (2), $c=20{\cdot}69$ (2) Å, $D_c=4{\cdot}44$ g cm^{-3}, $Z=4$, $\mu=136{\cdot}2$ cm^{-1}, F.W. 2996·8. Formula $Ag_{11}I_{13}C_9H_{24}N_2$. Space group *Ibam*.

The cell parameters were determined from the least-squares refinement of the angular settings of 25 high-order reflexions. 1084 independent reflexions were collected over the range $3° \le \theta \le 22°$ on a Philips PW1100 diffractometer in the ω–2θ mode with Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å) radiation. A scan speed of $0{\cdot}04°\theta$ s^{-1} and a scan width of $1{\cdot}2°\theta$ were used. Reflexion conditions: hkl $h+k+l=2n$, $0kl$ $k=2n$ ($l=2n$) and $h0l$ $h=2n$ ($l=2n$) indicated the two possible space groups *Ibam* and *Iba*2. The background was counted for half the scan time on each side of a reflexion. 375 reflexions were considered to be unobserved according to the criterion $I<1{\cdot}65\sigma(I)$, where $\sigma(I)=[(0{\cdot}02S)^2+S+B]^{1/2}$, S = scan count and B = background count. Three strong reflexions measured periodically throughout the data collection indicated no crystal decomposition. Lorentz and polarization factors were applied but no absorption corrections were made.

Solution of the structure

All computations for solving and refining the structure were executed with the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The structure was solved by direct methods with the tangent-refinement process incorporated in the program *TANGEN*. The distribution of E values indicated the centrosymmetric space group *Ibam*. Two origin-defining and two additional reflexions were selected for the phasing process. 5596 triplets were generated from this set of reflexions. After four cycles of tangent refinement, 211 reflexions with $E > 1{\cdot}3$ were phased. E maps were calculated for each of the four possible phase sets. The set which gave the correct solution was:

h	k	l	Phase angle
4	5	3	0
10	3	5	0
10	3	11	0
1	2	9	0

The E map revealed the positions of all the I^- and five disordered Ag^+ ions. The remaining Ag^+ ions were located in all the available tetrahedral sites from successive difference maps. However, the parameters of two of these disordered Ag^+ ions [*viz*. Ag(11) and Ag(12)] could not be refined owing to their low occupancies. Anisotropic refinement of the I^- and ten Ag^+ ions reduced R to 0·085. Population parameters of the Ag^+ ions were varied independently of their thermal parameters. Only the two N atoms of the hexamethylisopropylenediamine chain could be satisfactorily placed. In the centrosymmetric space group *Ibam* these two atoms are related by two of the three mutually perpendicular diad axes which intersect at $(\frac{1}{2},\frac{1}{2},\frac{1}{4})$. As a hexamethylisopropylenediamine chain contains no inherent twofold symmetry, it was clear from the N positions that the C atoms had to be disordered about these three diad axes. They could not be located. In an attempt to resolve the positions of the C atoms the structure was also refined in the non-centrosymmetric space

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

Anisotropic temperature factors are of the form:

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

Standard deviations are given in parentheses.

	Position	Population parameter	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	16(*k*)	1·0 (0)	1322 (3)	3942 (2)	3173 (2)	99 (3)	66 (2)	70 (2)	22 (2)	9 (2)	2 (2)
I(2)	16(*k*)	1·0 (0)	1907 (3)	3250 (2)	1181 (2)	89 (3)	73 (2)	70 (2)	18 (2)	−5 (2)	0 (2)
I(3)	8(*j*)	1·0 (0)	659 (4)	2178 (3)	5000 (0)	72 (3)	63 (3)	114 (4)	2 (3)	0 (0)	0 (0)
I(4)	8(*j*)	1·0 (0)	1782 (4)	626 (3)	0 (0)	76 (4)	60 (3)	154 (6)	13 (3)	0 (0)	0 (0)
I(5)	4(*d*)	1·0 (0)	0 (0)	5000 (0)	0 (0)	73 (4)	63 (4)	77 (5)	1 (4)	0 (0)	0 (0)
Ag(1)	16(*k*)	0·22 (1)	−103 (20)	3551 (13)	799 (11)	126 (21)	90 (16)	120 (20)	7 (15)	4 (17)	22 (14)
Ag(2)	16(*k*)	0·37 (6)	750 (19)	4312 (12)	1927 (27)	118 (14)	78 (10)	124 (26)	8 (9)	−8 (14)	13 (11)
Ag(3)	16(*k*)	0·38 (5)	1526 (29)	3647 (31)	4470 (14)	145 (22)	142 (28)	99 (15)	−28 (22)	18 (14)	13 (16)
Ag(4)	16(*k*)	0·15 (1)	1711 (23)	4935 (24)	755 (16)	110 (25)	100 (26)	119 (29)	2 (21)	34 (22)	1 (23)
Ag(5)	16(*k*)	0·35 (5)	2001 (24)	3183 (18)	4275 (11)	113 (17)	81 (14)	81 (12)	−6 (11)	24 (10)	−10 (9)
Ag(6)	16(*k*)	0·38 (7)	4468 (24)	550 (21)	3539 (43)	88 (14)	79 (13)	213 (59)	−14 (10)	38 (22)	−36 (21)
Ag(7)	8(*j*)	0·58 (5)	1375 (16)	2422 (18)	0 (0)	157 (16)	96 (19)	117 (12)	−24 (13)	0 (0)	0 (0)
Ag(8)	8(*j*)	0·28 (5)	992 (32)	3156 (50)	0 (0)	142 (33)	160 (66)	76 (20)	−42 (36)	0 (0)	0 (0)
Ag(9)	8(*j*)	0·38 (7)	1943 (45)	4245 (30)	0 (0)	97 (32)	94 (20)	124 (21)	−17 (20)	0 (0)	0 (0)
Ag(10)	8(*j*)	0·38 (7)	2627 (61)	3963 (22)	0 (0)	162 (53)	82 (16)	56 (12)	−21 (22)	0 (0)	0 (0)
Ag(11)†	8(*j*)	–	2400 (–)	2490 (–)	0 (0)	–	–	–	–	–	–
Ag(12)†	4(*b*)	–	0 (0)	5000 (0)	2500 (0)	–	–	–	–	–	–
						Isotropic U (Å^2)					
N(1)	8(*g*)	1·0 (0)	0 (0)	1194 (33)	2500 (0)	671					

† Parameters of these ions could not be refined owing to their low population parameters.

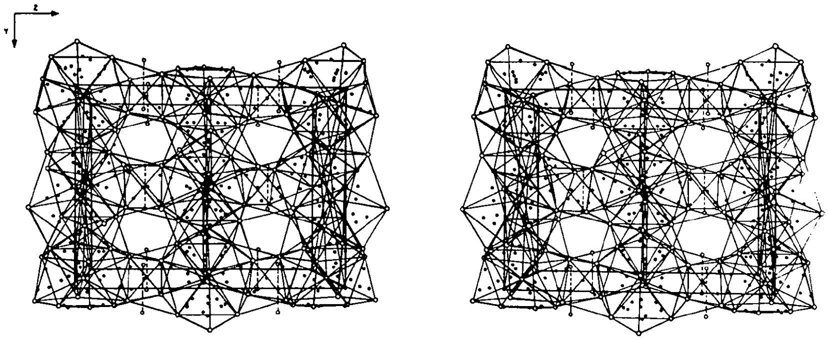

Fig. 1. A stereoscopic illustration of the structure. Black dots represent disordered silver ions in the iodide lattice. Solid lines represent I–I distances while broken lines show the N–N separation in each diamine chain.

group *Iba*2, in which the chain need only be disordered about one diad axis. Refinement in *Iba* 2 also only yielded the N positions. As the heavy-atom structure and N positions satisfied the symmetry of *Ibam*, this space group was used in the final refinement. The isotropic temperature factor obtained from a Wilson plot was assigned to N(1). In the final two cycles, all parameters except for the temperature factor of N(1) were varied simultaneously.

The final R was 0·080 for the 709 observed reflexions, where $R=\sum||F_o|-|F_c||/\sum|F_o|$. Unit weighting was applied. Scattering factors were those of Cromer & Mann (1968). A stereoscopic illustration of the structure is given in Fig. 1 (Johnson, 1965). A list of atomic parameters is given in Table 1. Interatomic distances are summarized in Table 2.*

Table 2. *Interatomic distances* (Å)

	Max.	Min.	Mean
I—I	5·31 (1)	4·16 (1)	4·60
Ag–I	3·23 (8)	2·73 (4)	2·86
N—I	5·28 (1)	4·88 (5)	5·07
N—N	3·74 (7)	–	–

Discussion

The crystal structures of several solid electrolytes containing AgI have been reported (Geller, 1967, 1972; Geller & Lind, 1970; Geller, Skarstad & Wilber, 1975; Coetzer, Kruger & Thackeray, 1976). The analyses have shown that conduction through these electrolytes occurs by the movement of Ag^+ ions through channels of face-sharing I tetrahedra and octahedra.

A stereoscopic illustration (Fig. 1) shows the I lattice of the unit cell. Ag^+ ions are located in tetrahedral sites. The I lattice in this structure consists of a network of face-sharing I tetrahedra. This network is made up of channels of these tetrahedra which extend in the **b** and **c** directions. The channels intersect at regular intervals to form circular bands of face-sharing tetrahedra, each band being centred on one of the non-origin symmetry centres (*e.g.* $\frac{1}{4},\frac{1}{4},\frac{1}{4}$). These circular bands are connected to one another along **a** by face-sharing tetrahedra to form spiral pathways for the Ag^+ ions. Movement of the Ag^+ ions can therefore take place in the **a**, **b** and **c** directions. The average I–I tetrahedral distance is 4·60 Å.

Holes exist in the I lattice, each of which contains one diamine chain. The central point of each of these holes coincides with the intersection of the three mutually perpendicular diad axes. The chain is extensively disordered about this point. Only the two N atoms could be satisfactorily placed. These atoms form octahedra with neighbouring I^- ions, the mean N–I distance in each octahedron being 5·07 (Å). The N–N distance of 3·74 Å is in good agreement with the value of 3·71 Å found in the parent hexamethylisopropylenediamine diiodide (Coetzer & Thackeray, 1976*c*).

Twelve iodide tetrahedra in the asymmetric unit give rise to 140 tetrahedra in the unit cell. The Ag^+ ions are located in all twelve tetrahedra and are extensively disordered. However, the parameters of Ag(11) and Ag(12) could not be satisfactorily refined owing to their low occupancies and were therefore excluded from the final refinement of the structure. The positional coordinates of these two disordered atoms were obtained from the final difference map and are reported in Table 1. The sum of the population parameters of the Ag^+ ions [excluding Ag(11) and Ag(12)] over the whole unit cell is 42·56. This is in good agreement with the value of 44 as implied by the formula $Ag_{11}I_{13}C_9H_{24}N_2$ which represents the contents of one quarter of the unit cell. Ag–I distances vary between 2·73 (4) and 3·23 (8) Å and have a mean value of 2·86 Å.

Results of conductivity measurements made on this system have been reported (Coetzer & Thackeray, 1976*a*). It was deduced from the graph of conductivity *vs* concentration of AgI in the electrolyte, that the electrolyte with the maximum conductivity of 0·03 $(\Omega\ \mathrm{cm})^{-1}$ at 20°C corresponded to a phase containing roughly 92 mol % AgI. The concentration of AgI in this compound is 91·7 mol % and it is likely that this structure represents the best conducting phase for this system.

References

Coetzer, J., Kruger, G. J. & Thackeray, M. M. (1976). *Acta Cryst.* B**32**, 1248–1251.

Coetzer, J. & Thackeray, M. M. (1975*a*). *Acta Cryst.* B**31**, 2341–2342.

Coetzer, J. & Thackeray, M. M. (1975*b*). *Acta Cryst.* B**31**, 2113–2114.

Coetzer, J. & Thackeray, M. M. (1976*a*). *Electrochim. Acta.* In the press.

Coetzer, J. & Thackeray, M. M. (1976*b*). To be published.

Coetzer, J. & Thackeray, M. M. (1976*c*). To be published.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Geller, S. (1967). *Science*, **157**, 310–312.

Geller, S. (1972). *Science*, **176**, 1016–1019.

Geller, S. & Lind, M. D. (1970). *J. Chem. Phys.* **52**, 5854–5861.

Geller, S., Skarstad, P. M. & Wilber, S. A. (1975). *J. Electrochem. Soc.* **122**, 332–338.

Johnson, C. K. (1965). *ORTEP.* Oak Ridge National Laboratory Report ORNL-3794.

Owens, B. B. (1970). *J. Electrochem. Soc.* **117**, 1536–1539.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). Univ. of Maryland Comput. Sci. Tech. Rep. TR-192.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31637 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.