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The Crystal Structure of $Ag_{31}I_{39}(C_8H_{22}N_2)_4$

BY J. COETZER, G. J. KRUGER AND M. M. THACKERAY

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

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$Ag_{31}I_{39}(C_8H_{22}N_2)_4$ is triclinic, space group $P\bar{1}$, with $a=16{\cdot}12$ (2), $b=11{\cdot}12$ (1), $c=19{\cdot}32$ (2) Å, $\alpha=96{\cdot}3$ (4), $\beta=91{\cdot}3$ (4), $\gamma=88{\cdot}3$ (4)°, $Z=1$. The final $R=0{\cdot}084$. The I ions form a three-dimensional network consisting of 102 face-sharing tetrahedra in the unit cell with the 31 Ag atoms distributed over 66 of these tetrahedral sites.

Introduction

N,N,N,N',N',N'-Hexamethylethylenediamine diiodide reacts with AgI in various stoichiometric proportions in the solid state to give a series of stable compounds. Many of these are extremely good ionic conductors. The maximum room-temperature conductivity [0·11 $(\Omega\ \text{cm})^{-1}$] for this series corresponds to a phase consisting of 97 mol % AgI (Coetzer & Thackeray, 1975*b*).

Single-crystal X-ray studies are presently being undertaken in order to study the structure–conductivity relationships in this series. Successful isolation and X-ray analyses have been carried out for two stable phases. These have formulae $Ag_2I_4C_8H_{22}N_2$ and $Ag_6I_8C_8H_{22}N_2$ corresponding to 67 and 86 mol % AgI, respectively (Coetzer & Thackeray, 1975*a*; Thackeray & Coetzer, 1975). The crystal structure of the compound described in this paper consists of 89 mol % AgI and shows a room-temperature conductivity of 0·01 $(\Omega\ \text{cm})^{-1}$.

Experimental

Slightly yellow crystals of $Ag_{31}I_{39}(C_8H_{22}N_2)_4$ were isolated from a solid-state reaction mixture of 90 mol % AgI and 10 mol % *N,N,N,N',N',N'*-hexamethylethylenediamine diiodide. The crystals were intergrown, making the isolation of a single specimen difficult. A small, roughly spherical crystal (0·06 mm diameter) was obtained for the measurement of cell dimensions and data collection on a Philips PW 1100 four-circle automatic diffractometer.

Crystal data

$Ag_{31}I_{39}(C_8H_{22}N_2)_4$, M.W. 8879·2, space group $P\bar{1}$, $a=16{\cdot}12$ (2), $b=11{\cdot}12$ (1), $c=19{\cdot}32$ (2) Å, $\alpha=96{\cdot}3$ (4), $\beta=91{\cdot}3$ (4), $\gamma=88{\cdot}3$ (4)°, $D_x=4{\cdot}29$ g cm^{-3}, $Z=1$.

Intensities for 6401 independent reflexions with $\theta \leq 20°$ were collected with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å), ω–2θ scan, scan width $=0{\cdot}8°$ and scan speed $=0{\cdot}04°$ s^{-1}. Background was counted for one half the total scanning time on each side of the reflexion. Of the 6401 intensities measured, 3650 were greater than $3\sigma(I)$, where $\sigma(I)$ is given by $[(0{\cdot}02S)^2+S+B]^{1/2}$. S is the scan count and B the total background count. During data collection the intensities of three reflexions were monitored every hour. The fluctuations were all less than 3%. The intensities were corrected for Lorentz and polarization factors but not for absorption ($\mu R=0{\cdot}39$).

Structure determination and refinement

The structure of the I lattice was solved by direct methods applied to the 400 reflexions with $|E| \geq 1{\cdot}4$. The multiple-solution technique was used as incorporated in the computer program *MULTAN* 74 (Declercq, Germain, Main & Woolfson, 1973). This program was modified to accept 400 reflexions and 2500 generated triplets. The starting set of phases was chosen to include three origin-defining and six additional reflexions. Assuming the structure to be centrosymmetric these additional reflexions were given phase angles of 0 or π resulting in the generation of 64 phase sets. The calculated figures of merit did not single out the correct solution but eight phase sets had the same best combined figure of merit. The E maps calculated from these eight sets produced only two different atomic arrangements. Structure factor calculations for the two trial structures, including I atoms in the positions indicated by the 30 strongest peaks in the E maps, generated R values of 0·52 and 0·48 respectively. Accepting the trial structure with lower R as correct, consecutive Fourier and difference maps led to the determination of the complete structure.

As the Ag atom positions were obviously not fully occupied, their population parameters were allowed to vary during refinement. Full-matrix least-squares refinement with isotropic temperature factors gave $R=0{\cdot}116$. During further refinement with anisotropic thermal parameters for the I and Ag atoms, computer storage limitations necessitated the use of a blocked matrix containing six blocks. No differential weighting was applied and the final R was 0·084.

The scattering factors were those of Cromer & Mann (1968). All crystallographic calculations, except for the application of direct methods, were done with

the X-RAY System of Crystallographic Programs (1972). The final atomic parameters are listed in Table 1. Selected interatomic distances and angles are given in Table 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31354 (34 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

The stereoscopic diagram in Fig. 1 shows the I lattice and the organic chains viewed along **b**. The Ag atoms are omitted in order to simplify the drawing. I atoms have been linked to illustrate their tetrahedral configurations.

The I atoms form an extensive network of face-sharing tetrahedra, the mean I···I interatomic distance being 4·64 Å. These tetrahedra link up to form a

Table 1. *Refined atomic parameters (fractional coordinates and anisotropic or isotropic temperature factors)*

Anisotropic thermal parameters are of the form $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$. Standard deviations are given in parentheses. All parameters, except population parameters, are $\times 10^4$.

	x	*y*	*z*	p.p.	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	2440 (3)	507 (4)	4154 (3)	1·0	753 (38)	432 (31)	442 (31)	50 (27)	76 (26)	40 (24)
I(2)	7438 (3)	4820 (4)	1003 (2)	1·0	439 (31)	466 (31)	417 (30)	36 (24)	11 (23)	83 (24)
I(3)	2656 (3)	3573 (4)	2708 (2)	1·0	398 (29)	467 (31)	432 (29)	−13 (24)	3 (23)	61 (23)
I(4)	6078 (3)	2943 (4)	6757 (2)	1·0	466 (30)	403 (29)	352 (27)	−67 (23)	39 (22)	−16 (22)
I(5)	9009 (3)	3028 (4)	6617 (2)	1·0	436 (31)	522 (32)	434 (30)	−23 (25)	−49 (23)	142 (24)
I(6)	9058 (3)	1163 (5)	269 (3)	1·0	588 (36)	566 (36)	484 (33)	21 (28)	94 (26)	21 (27)
I(7)	7998 (3)	1718 (5)	2323 (3)	1·0	648 (37)	506 (34)	525 (34)	104 (28)	189 (28)	87 (27)
I(8)	6162 (3)	1349 (5)	305 (3)	1·0	524 (33)	600 (36)	465 (31)	−16 (27)	0 (25)	13 (26)
I(9)	2070 (3)	2243 (4)	424 (2)	1·0	429 (32)	527 (33)	375 (28)	−56 (25)	15 (23)	42 (24)
I(10)	5694 (3)	3650 (5)	2761 (3)	1·0	429 (32)	603 (37)	493 (33)	80 (27)	−25 (25)	118 (27)
I(11)	2096 (3)	6729 (4)	1248 (3)	1·0	449 (31)	449 (31)	526 (32)	−30 (24)	−17 (24)	118 (25)
I(12)	0	5000	0	1·0	880 (64)	728 (59)	540 (51)	60 (49)	29 (44)	163 (43)
I(13)	7503 (3)	3188 (4)	4692 (2)	1·0	516 (32)	316 (28)	357 (28)	−57 (23)	−56 (23)	28 (22)
I(14)	789 (3)	190 (4)	6043 (2)	1·0	556 (33)	422 (30)	399 (29)	10 (25)	95 (24)	29 (23)
I(15)	1 (3)	4092 (4)	2001 (2)	1·0	712 (37)	531 (33)	450 (33)	41 (28)	66 (27)	116 (26)
I(16)	860 (3)	2100 (4)	8446 (2)	1·0	412 (30)	493 (32)	320 (27)	12 (24)	11 (22)	2 (23)
I(17)	4381 (3)	4744 (5)	915 (2)	1·0	450 (33)	628 (36)	400 (31)	−20 (27)	84 (25)	78 (26)
I(18)	1944 (3)	3943 (5)	6629 (3)	1·0	549 (36)	659 (38)	469 (31)	−148 (29)	137 (26)	−6 (27)
I(19)	964 (3)	477 (5)	2200 (3)	1·0	371 (31)	665 (38)	675 (37)	−102 (27)	96 (26)	47 (30)
I(20)	3807 (3)	194 (5)	6246 (3)	1·0	703 (37)	473 (33)	405 (30)	−147 (27)	−124 (26)	98 (25)
Ag(1)	2360 (4)	9598 (7)	5470 (4)	0·86 (2)	646 (54)	950 (63)	596 (51)	116 (40)	−62 (35)	174 (39)
Ag(2)	2360 (7)	7833 (10)	9078 (6)	0·69 (2)	551 (83)	778 (94)	985 (100)	−11 (61)	−90 (62)	52 (67)
Ag(3)	2520 (4)	7960 (7)	4054 (4)	0·95 (2)	815 (61)	747 (58)	709 (56)	−99 (41)	134 (40)	151 (39)
Ag(4)	9219 (6)	7607 (9)	3002 (4)	0·93 (3)	1221 (92)	994 (82)	589 (64)	−389 (62)	−20 (52)	226 (51)
Ag(5)	9297 (5)	129 (8)	2521 (4)	0·97 (2)	600 (67)	752 (72)	675 (69)	39 (48)	105 (47)	−12 (48)
Ag(6)	387 (14)	6126 (21)	1344 (13)	0·32 (2)	774 (180)	695 (179)	1136 (197)	−91 (124)	61 (128)	52 (192)
Ag(7)	547 (21)	1935 (34)	1072 (18)	0·24 (3)	929 (272)	1343 (334)	1186 (301)	−93 (210)	57 (196)	585 (231)
Ag(8)	988 (16)	6429 (26)	9205 (16)	0·27 (2)	428 (192)	779 (234)	1033 (258)	4 (146)	77 (150)	−256 (170)
Ag(9)	7625 (7)	3885 (11)	7380 (6)	0·74 (3)	824 (104)	827 (103)	632 (90)	152 (72)	−28 (67)	122 (67)
Ag(10)	6810 (4)	1988 (6)	3410 (3)	1·03 (3)	948 (62)	669 (54)	602 (50)	−111 (40)	41 (38)	161 (36)
Ag(11)	5921 (8)	3487 (12)	1245 (7)	0·67 (3)	742 (111)	794 (114)	804 (110)	−38 (78)	222 (77)	−122 (77)
Ag(12)	5902 (6)	5198 (9)	7647 (4)	0·82 (2)	814 (79)	852 (80)	504 (65)	−196 (55)	52 (48)	61 (49)
Ag(13)	1499 (30)	5378 (48)	2229 (22)	0·21 (3)	1442 (430)	2024 (519)	782 (325)	284 (331)	10 (257)	−370 (289)
Ag(14)	2155 (46)	8382 (75)	7771 (41)	0·08 (2)	104 (573)	479 (684)	367 (597)	−149 (427)	43 (392)	−75 (435)
Ag(15)	2364 (20)	7462 (34)	9849 (23)	0·20 (2)	181 (250)	471 (304)	1454 (440)	−252 (193)	150 (223)	−127 (250)
Ag(16)	2609 (15)	4579 (19)	546 (12)	0·31 (2)	779 (193)	459 (162)	903 (189)	35 (121)	−59 (132)	−215 (120)
Ag(17)	3422 (26)	6990 (60)	8431 (25)	0·13 (2)	241 (318)	1603 (626)	644 (371)	183 (300)	−49 (22)	−726 (339)
Ag(18)	1396 (9)	2698 (15)	1755 (7)	0·70 (3)	833 (128)	1165 (152)	842 (124)	164 (97)	115 (87)	63 (96)
Ag(19)	3510 (23)	5355 (34)	2134 (17)	0·22 (2)	1300 (334)	1177 (332)	524 (245)	−542 (235)	241 (194)	68 (197)
Ag(20)	725 (13)	8628 (21)	1091 (10)	0·49 (3)	1059 (192)	1483 (229)	689 (157)	−426 (149)	306 (123)	−120 (131)
Ag(21)	6676 (39)	3748 (73)	9815 (45)	0·10 (2)	1569 (473)	949 (687)	1551 (775)	110 (384)	−17 (407)	−746 (531)
Ag(22)	117 (16)	9741 (23)	1004 (11)	0·38 (3)	1417 (248)	1168 (220)	645 (169)	−243 (164)	−151 (139)	245 (134)
Ag(23)	330 (11)	2701 (17)	602 (11)	0·51 (3)	613 (149)	947 (168)	1486 (196)	−252 (111)	−75 (117)	145 (127)
Ag(24)	552 (12)	6363 (18)	1824 (12)	0·60 (3)	833 (173)	923 (182)	1660 (236)	8 (124)	212 (140)	480 (148)
Ag(25)	984 (12)	9441 (15)	3392 (9)	0·54 (3)	1338 (185)	691 (131)	1024 (158)	−397 (111)	−184 (118)	249 (102)
Ag(26)	1738 (10)	5741 (14)	7719 (7)	0·72 (3)	1390 (144)	1061 (134)	905 (121)	191 (97)	−206 (91)	−298 (89)
Ag(27)	2707 (12)	4251 (16)	1243 (10)	0·52 (3)	1082 (178)	682 (148)	998 (175)	−251 (114)	−58 (122)	18 (111)
Ag(28)	4074 (16)	6106 (24)	9695 (15)	0·42 (3)	829 (239)	805 (237)	1223 (264)	9 (164)	−167 (173)	−50 (172)
Ag(29)	8289 (27)	5912 (37)	8408 (18)	0·14 (2)	874 (362)	617 (327)	261 (253)	473 (241)	−413 (207)	−72 (194)
Ag(30)	2491 (18)	5826 (22)	7474 (18)	0·38 (3)	1233 (273)	502 (204)	1743 (355)	−192 (165)	−101 (216)	9 (186)
Ag(31)	9192 (37)	1927 (43)	7872 (26)	0·09 (2)	654 (479)	112 (349)	210 (361)	41 (269)	175 (278)	−113 (233)
Ag(32)	9544 (41)	7634 (61)	4 (31)	0·12 (2)	491 (547)	769 (601)	867 (469)	−398 (409)	82 (351)	−493 (372)
Ag(33)	8348 (16)	5397 (23)	9875 (16)	0·46 (3)	1525 (241)	1561 (239)	2588 (339)	309 (168)	749 (205)	1211 (218)

Table 1 (*cont.*)

	x	*y*	*z*	*B*
C(1)	0·3107 (74)	0·1432 (107)	0·8246 (61)	5·4 (3·7)
C(2)	0·4125 (54)	0·2800 (81)	0·7970 (45)	5·0 (2·5)
C(3)	0·4138 (46)	0·2245 (68)	0·9170 (38)	4·1 (2·0)
C(4)	0·4483 (57)	0·0658 (82)	0·8251 (47)	4·4 (2·6)
C(5)	0·5424 (48)	0·0881 (68)	0·8326 (38)	3·5 (2·0)
C(6)	0·5855 (50)	0·8735 (73)	0·8556 (42)	3·2 (2·2)
C(7)	0·5789 (52)	0·9144 (77)	0·7335 (44)	5·0 (2·3)
C(8)	0·6893 (64)	−0·0100 (93)	0·8150 (53)	7·6 (3·1)
C(9)	0·3847 (54)	0·3737 (80)	0·4321 (46)	5·2 (2·5)
C(10)	0·3952 (51)	0·3336 (74)	0·5544 (42)	5·1 (2·3)
C(11)	0·4818 (54)	0·2274 (80)	0·4784 (45)	5·5 (2·5)
C(12)	0·5127 (54)	0·4319 (75)	0·4971 (45)	2·8 (2·4)
C(13)	−0·0079 (87)	0·3183 (129)	0·3789 (72)	12·2 (4·8)
C(14)	0·0323 (57)	0·2781 (83)	0·5013 (47)	5·3 (2·7)
C(15)	0·1233 (59)	0·3725 (85)	0·4288 (49)	5·6 (2·8)
C(16)	0·0083 (139)	0·4712 (194)	0·4713 (95)	20·0 (8·2)
N(1)	0·3940 (36)	0·1867 (52)	0·8438 (30)	3·1 (1·5)
N(2)	0·5973 (41)	−0·0193 (59)	0·8061 (33)	4·7 (1·8)
N(3)	0·4416 (39)	0·3553 (56)	0·4931 (33)	4·9 (1·8)
N(4)	0·0428 (35)	0·3540 (51)	0·4437 (29)	2·3 (1·5)

continuous column about the centre at the origin extending in the **b** direction. This results in a large number of channels of face-sharing tetrahedra, allowing for the rapid diffusion of Ag ions through the I lattice (Foley, 1969). The three-dimensional network of I tetrahedra in the **a** and **c** directions is interrupted by the hexamethylethylenediamine ions. In the **c** direction the columns of I tetrahedra are linked by single strands of face-sharing tetrahedra, providing a pathway for Ag ions to diffuse from one column to another. In the **a** direction, however, two columns are linked together by side-sharing tetrahedra, effectively blocking Ag diffusion in this direction. Ag ions can only move in this direction if they pass through a tetrahedron or an octahedron formed by a combination of both I and N atoms.

The N atoms of the amines are located in such a way that they form tetrahedra or octahedra with the I, resulting in one continuous lattice of face-sharing tetrahedra and octahedra.

The 31 Ag atoms in the unit cell are extensively disordered. They are distributed over 66 of the 102 tetrahedral sites with site occupancies varying between 8 and 100%. These values (Table 1) were obtained from the least-squares refinement of the atomic parameters. During refinement, no restraints were placed on the magnitudes of the population parameters. The sum of the values shows the unit cell to contain 31·6 Ag ions compared to the 31 required on the basis of stoichiometry. The remaining 36 sites are vacant. Fig. 2

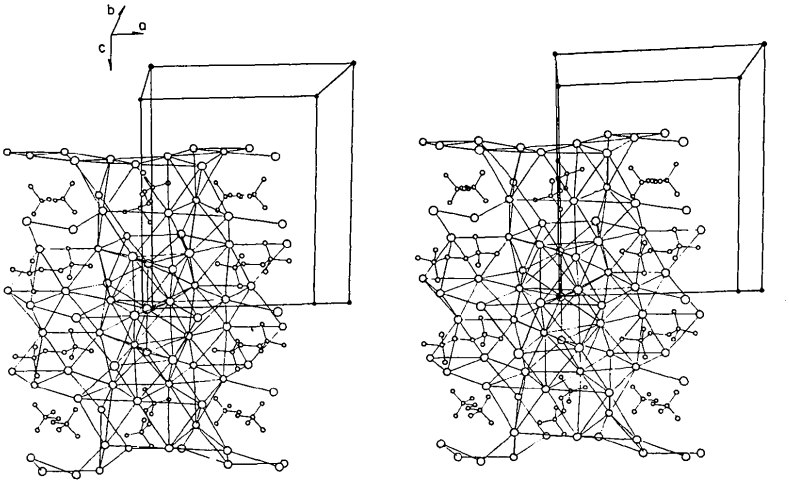

Fig. 1. Stereoscopic drawing showing the iodide lattice and the organic diamines of $Ag_{31}I_{39}(C_8H_{22}N_2)_4$ viewed along **b**.

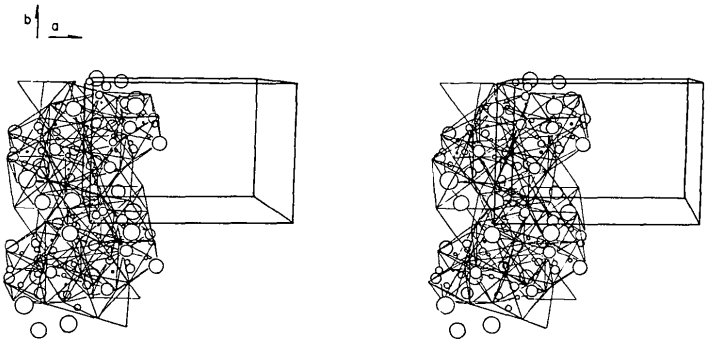

Fig. 2. Stereoscopic view of the AgI lattice along **c**.

shows a diagram of the AgI lattice viewed along **c**. The column of face-sharing tetrahedra is clearly seen.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Standard deviations in parentheses.

I···I interatomic distances in iodide tetrahedra (average estimated standard deviation = 0·01 Å)

I(1)–I(3)	4·66	I(4)–I(5)	4·74
–I(4)	4·66	–I(10)	4·70
–I(5)	4·71	–I(11)	4·78
–I(13)	4·88	–I(13)	4·68
–I(14)	4·61	–I(17)	4·98
–I(19)	4·42	–I(20)	4·85
–I(20)	4·60		
		I(5)–I(11)	4·50
I(2)–I(6)	4·86	–I(13)	4·41
–I(7)	4·57	–I(14)	4·27
–I(8)	4·49	–I(15)	4·26
–I(9)	4·59	–I(16)	4·75
–I(10)	4·77	–I(18)	4·86
–I(11)	4·57	–I(19)	4·73
–I(12)	4·62		
–I(16)	4·47	I(6)–I(7)	4·33
–I(17)	4·73	–I(8)	4·66
–I(18)	4·72	–I(9)	4·31
		–I(11)	4·30
I(3)–I(4)	4·44	–I(12)	4·65
–I(5)	4·65	–I(15)	4·66
–I(9)	4·58	–I(16)	4·61
–I(10)	4·89	–I(19)	4·89
–I(11)	4·79		
–I(15)	4·50		
–I(17)	4·80		
–I(19)	4·46		
I(7)–I(8)	4·82	I(11)–I(12)	4·44
–I(10)	4·28	–I(15)	4·87
–I(13)	4·76	–I(16)	4·91
–I(14)	4·38	–I(17)	4·24
–I(15)	4·32	–I(19)	4·69
–I(16)	4·68		
–I(19)	4·93	I(12)–I(15)	4·08
–I(20)	4·75	–I(16)	4·35
I(8)–I(9)	4·93	I(13)–I(14)	4·69
–I(10)	5·19	–I(18)	4·41
–I(11)	4·85	–I(20)	4·54
–I(17)	4·75		
		I(14)–I(16)	4·88
I(9)–I(11)	5·07	–I(18)	4·63
–I(12)	4·58	–I(19)	4·59
–I(15)	4·82	–I(20)	4·85
–I(16)	4·23		
–I(17)	4·72	I(15)–I(16)	4·58
–I(19)	4·55	–I(18)	4·49
		–I(19)	4·32
I(10)–I(13)	4·73		
–I(17)	4·37	I(16)–I(18)	4·64
–I(18)	4·76	–I(19)	4·23
–I(20)	4·91		
		I(18)–I(20)	5·05

Distances between Ag sites in face-sharing tetrahedra vary between 1·0 and 2·2 Å.

The mean I···I···I interatomic angle in iodide tetrahedra is 59·9°.

Table 2 (*cont.*)

Organic diamines (average estimated standard deviations in bond lengths and angles are 0·10 Å and 1·8°, respectively); primed atoms are related to unprimed equivalents by a centre of symmetry.

N(1)–C(1)	1·47	N(3)—C(11)	1·55
–C(2)	1·49	–C(12)	1·44
–C(3)	1·46	N(4)—C(13)	1·50
–C(4)	1·59	–C(14)	1·48
N(2)–C(5)	1·52	–C(15)	1·36
–C(6)	1·62	–C(16)	1·57
–C(7)	1·54	C(4)—C(5)	1·54
–C(8)	1·49	C(12)–C(12′)	1·55
N(3)–C(9)	1·51	C(16)–C(16′)	1·25
–C(10)	1·46		

C(1)–N(1)–C(2)	107·0	C(9)—N(3)—C(10)	111·6
C(1)–N(1)–C(3)	119·0	C(9)—N(3)—C(11)	106·8
C(1)–N(1)–C(4)	100·5	C(9)—N(3)—C(12)	112·8
C(2)–N(1)–C(3)	113·2	C(10)–N(3)—C(11)	97·5
C(2)–N(1)–C(4)	111·3	C(10)–N(3)—C(12)	122·6
C(3)–N(1)–C(4)	105·0	C(11)–N(3)—C(12)	102·4
C(5)–N(2)–C(6)	108·4	C(13)–N(4)—C(14)	115·2
C(5)–N(2)–C(7)	118·9	C(13)–N(4)—C(15)	111·6
C(5)–N(2)–C(8)	118·9	C(13)–N(4)—C(16)	98·4
C(6)–N(2)–C(7)	101·5	C(14)–N(4)—C(15)	114·4
C(6)–N(2)–C(8)	97·3	C(14)–N(4)—C(16)	100·9
C(7)–N(2)–C(8)	108·1	C(15)–N(4)—C(16)	115·0
N(1)–C(4)–C(5)	112·2	N(3)—C(12)–C(12′)	112·2
N(2)–C(5)–C(4)	114·5	N(4)—C(16)–C(16′)	121·4

The sizes of the Ag atoms have been drawn on a relative scale to reflect the magnitudes of the individual population parameters. The shortest distances between Ag sites in face-sharing tetrahedra vary between 1·0 and 2·2 Å, Since the distance between atoms in metallic Ag is 2·9 Å it is evident that adjacent Ag sites cannot be occupied simultaneously.

Three crystallographically non-equivalent diamine molecules are found. Two of these lie on centres at $(0,\frac{1}{2},\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, respectively, while the third lies in a general position, retaining its centrosymmetric conformation.

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