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Silver iodide – Piperazinium – 4-Dimethylformamide*

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Abstract. $Ag_{10}I_{12}.C_4H_{12}N_2.4C_3H_7NO$, monoclinic, $P2_1/c$, $a=14{\cdot}52$ (7), $b=25{\cdot}06$ (9), $c=7{\cdot}84$ (4) Å, $\beta=100{\cdot}3$ (4)°, $Z=2$, $D_c=3{\cdot}53$, $D_m=3{\cdot}51$ g cm^{-3}. Final $R=0{\cdot}051$. The iodine atoms form a three-dimensional structure of face-sharing tetrahedra with silver atoms occupying one quarter of the tetrahedral holes in the unit cell.

Introduction. The complex was prepared from stoichiometric quantities of AgI and piperazine dihydroiodide in dimethylformamide (DMF). Colourless needles of $Ag_{10}I_{12}.C_4H_{12}N_2.4DMF$ were obtained by recrystallization from DMF solution. Oscillation, Weissenberg and precession photographs showed the crystals to be monoclinic with space group $P2_1/c$.

A crystal ground to roughly spherical shape with a diameter of 0·03 mm was used to measure the cell parameters and the intensities of 2609 independent reflexions on a Philips PW 1100 four-circle automatic diffractometer. The data were collected to a maximum θ of 20° with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å, ω–2θ scan, scan width 1·2°, scan speed 0·04° s^{-1}). Of the intensities measured, 2198 were considered observed, with $I/\sigma(I)>1{\cdot}65$, where $\sigma(I)=[(0{\cdot}02S)^2+S+B]^{1/2}|$, S = scan count and B = total background count. The background was counted for one half of the total scanning time on each side of the reflexion. Corrections were made for Lorentz and polarization factors but not for absorption ($\mu=100{\cdot}2$ cm^{-1}).

The structure was solved by the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1966) with the program *PHASE* from the X-RAY 72 set of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). These programs were used for all other computations. A full-matrix least-squares refinement of the trial parameters, with individual anisotropic thermal factors and unit weights assigned to all reflexions, led to an R of 0·051 [$R=\sum(|F_o|-|F_c|)/\sum|F_o|$].† The scattering factors were those of Cromer & Mann (1968). Table 1

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30721 (19 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates and anisotropic temperature factors* $\times 10^4$

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.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	1806 (2)	3639 (1)	1472 (3)	895 (19)	898 (19)	485 (15)	4 (16)	193 (13)	−61 (14)
Ag(2)	−70 (2)	2835 (1)	871 (3)	940 (20)	723 (17)	570 (16)	12 (15)	275 (14)	−41 (13)
Ag(3)	637 (2)	1621 (1)	1052 (3)	753 (17)	739 (17)	483 (14)	69 (13)	155 (12)	72 (12)
Ag(4)	2865 (2)	1629 (1)	1907 (3)	751 (17)	711 (17)	484 (14)	−11 (13)	97 (12)	61 (12)
Ag(5)	3640 (2)	2826 (1)	2137 (2)	936 (19)	684 (17)	460 (14)	4 (14)	59 (13)	26 (12)
I(1)	1793 (1)	2483 (1)	5104 (2)	533 (11)	458 (10)	122 (8)	−15 (8)	107 (7)	−10 (7)
I(2)	−933 (1)	1990 (1)	2357 (2)	537 (12)	673 (13)	343 (10)	−1 (10)	118 (9)	3 (9)
I(3)	118 (1)	3812 (1)	2666 (2)	748 (14)	557 (12)	317 (10)	125 (10)	145 (9)	11 (9)
I(4)	1744 (1)	863 (1)	3193 (2)	676 (12)	466 (11)	298 (10)	29 (10)	111 (9)	15 (8)
I(5)	3476 (1)	3801 (1)	3870 (2)	726 (14)	560 (13)	289 (10)	−150 (10)	172 (9)	−17 (8)
I(6)	4501 (1)	1973 (1)	4189 (2)	553 (12)	598 (12)	300 (9)	62 (9)	76 (9)	20 (9)
O(1)	6639 (40)	4684 (18)	6963 (83)	2003 (536)	1342 (373)	3350 (748)	−278 (357)	2407 (589)	−499 (407)
O(2)	6092 (38)	4251 (14)	2510 (65)	1141 (373)	329 (211)	958 (307)	95 (226)	−41 (250)	196 (228)
N(1)	8189 (30)	4671 (11)	6915 (46)	1395 (332)	442 (180)	1088 (266)	194 (202)	568 (257)	−68 (171)
N(2)	4157 (21)	4688 (12)	43 (50)	547 (205)	454 (199)	1314 (324)	−24 (167)	457 (219)	−76 (206)
N(3)	6719 (22)	3382 (15)	2892 (38)	583 (204)	1371 (325)	643 (199)	−291 (217)	−217 (161)	23 (202)
C(1)	4820 (23)	4588 (11)	−1316 (35)	900 (246)	466 (186)	432 (183)	−135 (178)	201 (171)	−196 (151)
C(2)	4721 (18)	4896 (11)	1636 (32)	471 (173)	576 (192)	349 (164)	−377 (151)	265 (138)	−253 (143)
C(3)	8571 (54)	4575 (22)	8607 (67)	6176 (933)	1363 (438)	483 (353)	1510 (504)	−458 (444)	1 (317)
C(4)	8865 (40)	4720 (21)	5813 (76)	1706 (492)	1389 (438)	1854 (542)	−92 (373)	1206 (454)	−375 (394)
C(5)	7289 (43)	4737 (21)	6267 (111)	1031 (420)	887 (401)	3624 (1063)	9 (348)	136 (541)	−800 (520)
C(6)	7394 (43)	3511 (21)	1775 (100)	1507 (515)	1026 (415)	2968 (849)	46 (371)	600 (564)	−97 (475)
C(7)	6137 (27)	3845 (28)	2930 (72)	528 (246)	2996 (736)	2010 (567)	399 (430)	−33 (293)	−1720 (564)
C(8)	6745 (40)	3856 (18)	3567 (71)	1862 (521)	840 (327)	1763 (500)	−214 (329)	−362 (399)	826 (352)

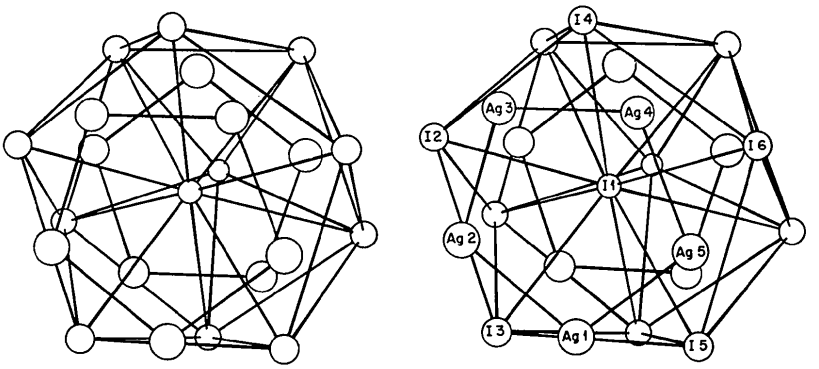

Fig. 1. Stereoscopic drawing showing the AgI lattice.

lists the final atomic parameters. Interatomic distances and angles are given in Table 2.

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

Standard deviations are in parentheses. Primed atoms are related to the unprimed equivalents by the glide plane at $y=\frac{1}{4}$.

Ag–I			
Ag(1)–I(1)	3·00 (2)	Ag(3)–I(3)	2·84 (1)
Ag(1)–I(3)	2·81 (1)	Ag(3)–I(4)	2·84 (1)
Ag(1)–I(4)′	2·84 (1)	Ag(4)–I(1)	2·93 (1)
Ag(1)–I(5)	2·82 (1)	Ag(4)–I(4)	2·82 (1)
Ag(2)–I(1)	2·98 (1)	Ag(4)–I(5)′	2·89 (1)
Ag(2)–I(2)	2·82 (1)	Ag(4)–I(6)	2·84 (1)
Ag(2)–I(2)′	2·85 (1)	Ag(5)–I(1)	2·97 (1)
Ag(2)–I(3)	2·81 (1)	Ag(5)–I(5)	2·83 (1)
Ag(3)–I(1)	2·98 (1)	Ag(5)–I(6)	2·83 (1)
Ag(3)–I(2)	2·82 (1)	Ag(5)–I(6)′	2·86 (1)
Ag–Ag ring		I–I ring	
Ag(1)–Ag(2)	3·35 (2)	I(2)–I(3)	4·80 (2)
Ag(2)–Ag(3)	3·21 (2)	I(3)–I(5)	4·80 (2)
Ag(3)–Ag(4)	3·18 (2)	I(4)–I(6)	4·82 (2)
Ag(4)–Ag(5)	3·20 (2)	I(4)–I(2)	4·75 (2)
Ag(5)–Ag(1)	3·32 (2)	I(5)–I(6)	4·81 (2)
I(1)–I distance in Ag-occupied tetrahedra			
I(1)–I(2)′	4·33 (2)	I(1)–I(5)′	4·32 (1)
I(1)–I(3)′	4·35 (1)	I(1)–I(6)′	4·32 (2)
I(1)–I(4)′	4·32 (2)		
I(1)–I distance in unoccupied tetrahedra			
I(1)–I(2)	4·80 (2)	I(1)–I(5)	4·74 (1)
I(1)–I(3)	4·71 (1)	I(1)–I(6)	4·81 (2)
I(1)–I(4)	4·81 (2)		
O(1)–C(5)	1·18 (10)	N(2)–C(2)	1·46 (4)
O(2)–C(7)	1·07 (8)	N(3)–C(6)	1·46 (8)
N(1)–C(3)	1·36 (6)	N(3)–C(7)	1·44 (7)
N(1)–C(4)	1·42 (8)	N(3)–C(8)	1·42 (6)
N(1)–C(5)	1·32 (7)	C(1)–C(2)	1·50 (4)
N(2)–C(1)	1·58 (5)		
I(1)–Ag(1)–I(4)	95·2 (3)	I(1)–Ag(3)–I(3)	97·0 (3)
I(1)–Ag(1)–I(5)	108·8 (3)	I(2)–Ag(3)–I(3)	111·6 (3)
I(1)–Ag(1)–I(3)	108·2 (3)	I(2)–Ag(3)–I(1)	111·9 (3)
I(3)–Ag(1)–I(4)	110·2 (3)	I(4)–Ag(3)–I(3)	109·0 (3)
I(3)–Ag(1)–I(5)	116·9 (3)	I(4)–Ag(3)–I(1)	111·6 (3)
I(4)–Ag(1)–I(5)	115·1 (3)	I(4)–Ag(3)–I(2)	114·5 (3)
I(1)–Ag(2)–I(2)′	96·0 (3)	I(1)–Ag(4)–I(5)	95·8 (3)
I(2)–Ag(2)–I(2)′	111·4 (3)	I(4)–Ag(4)–I(1)	113·5 (3)
I(2)–Ag(2)–I(1)	111·6 (3)	I(4)–Ag(4)–I(5)	108·8 (3)
I(3)–Ag(2)–I(2)′	109·7 (3)	I(4)–Ag(4)–I(6)	116·9 (3)
I(3)–Ag(2)–I(1)	108·9 (3)	I(6)–Ag(4)–I(1)	112·7 (3)
I(3)–Ag(2)–I(2)	117·2 (3)	I(6)–Ag(4)–I(5)	106·6 (3)

Discussion. The geometry of the AgI lattice and the atomic numbering is shown in Fig. 1 (*ORTEP*, Johnson, 1965).

Each silver atom is tetrahedrally surrounded by four iodine atoms. The iodines form a three-dimensional array of face-sharing tetrahedra, showing an average I···I distance of 4·44 Å. 40 iodine tetrahedra are thus formed in the unit cell. Ten of these enclose silver atoms with the remainder vacant. The silver atoms are stacked as five-membered rings, oriented approximately in the *ab* plane and recurring half a cell translation away in the **c** direction. Consecutive rings are staggered in the **c** direction. The average Ag···Ag distance in the ring is 3·25 Å.

I(1) is close to the line joining the centres of neighbouring five-membered rings of Ag atoms. The other five iodines in the asymmetric unit form a regular five-membered ring, half-way between two rings of silver atoms. The staggering pattern is also found for consecutive rings of iodine atoms.

The average I(1)···I(ring) distance of 4·26 Å in empty tetrahedra is slightly shorter than the average I(1)···I(ring) distance of 4·63 Å in Ag-filled tetrahedra. The average Ag···I(1) distance of 2·97 Å is somewhat longer than the average Ag···I(ring) distance of 2·83 Å.

The piperazine dihydronium ion is located on the symmetry centre at $(\frac{1}{2},\frac{1}{2},0)$ and only one half of it contributes to the asymmetric unit. The molecular formula $Ag_{10}I_{12}.C_4H_{12}N_2$ thus contains two asymmetric units.

The crystals are stable in air at room temperature and include two molecules of DMF in the asymmetric unit.

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