

Acta Cryst. (1975). B31, 2115**Silver Iodide–Piperazinium–(Dimethyl Sulphoxide)₄**

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Abstract. Ag₄I₆C₄H₁₂N₂·4C₂H₆SO, triclinic, $P\bar{1}$, $a = 12.96$ (2), $b = 11.54$ (2), $c = 6.54$ (1) Å, $\alpha = 93.8$ (2), $\beta = 100.7$ (3), $\gamma = 104.2$ (3)°, $Z = 1$, $D_m = 2.42$, $D_x = 2.44$ g cm⁻³. Final $R = 0.066$. The AgI lattice consists of linear chains of Ag atoms extending in the c direction, with each Ag tetrahedrally surrounded by I atoms. The I tetrahedra are linked together by double edge sharing.

Introduction. Stoichiometric quantities of AgI and piperazine dihydroiodide react in dimethyl sulphoxide (DMSO) to yield colourless needles of Ag₄I₆C₄H₁₂N₂·4DMSO. Oscillation, Weissenberg and precession photographs showed the crystals to be triclinic.

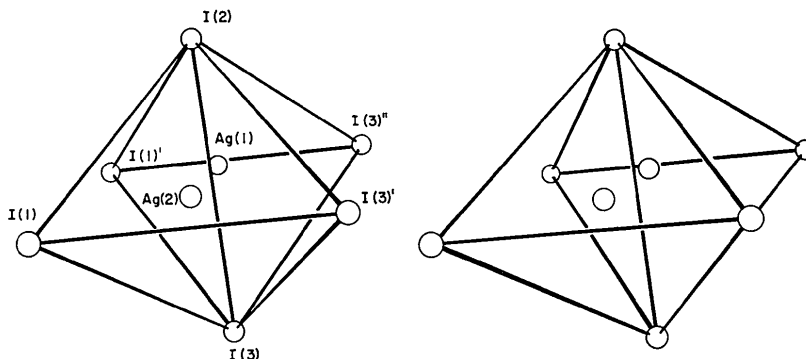
The cell parameters, and intensities for 1727 independent reflexions, were measured with a small needle (0.03 × 0.04 × 0.1 mm) on a Philips PW1100 four-circle automatic diffractometer. Details of the data collection are: maximum θ of 20°, graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), ω -2 θ scan, scan width = 1.2°, scan speed = 0.04° s⁻¹. The background was counted for one half the total scanning time on each side of the reflexion. 1363 reflexions were considered to be observed, with $I/\sigma(I) > 3.0$, where $\sigma(I) = [(0.025)^2 + S + B]^{1/2}$, S = scan count and B = total background count. The intensities were corrected for Lorentz and polarization factors but not for absorption.

The trial structure was found by the symbolic addition procedure for centrosymmetric crystals (Karle &

Table 1. *Refined atomic parameters* ($\times 10^4$)

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)	3621 (2)	4023 (3)	9361 (5)	792 (22)	669 (20)	682 (20)	88 (16)	183 (17)	-50 (16)
Ag(2)	3592 (3)	3999 (3)	4425 (5)	823 (23)	625 (19)	696 (21)	73 (16)	115 (17)	56 (16)
I(1)	1191 (2)	4455 (2)	1324 (4)	590 (16)	569 (16)	650 (16)	113 (12)	127 (13)	18 (12)
I(2)	2908 (2)	1946 (2)	6418 (3)	525 (15)	479 (14)	466 (14)	-16 (11)	117 (12)	-32 (11)
I(3)	4525 (2)	6170 (2)	7434 (4)	551 (14)	409 (13)	489 (14)	27 (11)	109 (11)	-26 (10)
S(1)	1237 (21)	-2317 (16)	6191 (28)	4192 (277)	1039 (129)	1010 (135)	1163 (159)	233 (160)	77 (105)
S(2)	3470 (7)	-808 (8)	3292 (14)	454 (60)	562 (27)	583 (60)	123 (45)	98 (48)	-4 (46)
O(1)	569 (20)	-1316 (30)	5989 (34)	720 (180)	99 (279)	568 (145)	90 (191)	223 (130)	-110 (157)
O(2)	2269 (17)	-1074 (18)	2379 (35)	499 (153)	484 (139)	714 (162)	240 (116)	164 (127)	60 (117)
N(1)	587 (19)	27 (20)	2151 (34)	409 (158)	413 (152)	282 (149)	102 (128)	92 (128)	89 (122)
C(1)	288 (24)	1068 (24)	-1066 (45)	415 (198)	232 (166)	368 (182)	-62 (150)	78 (160)	-34 (144)
C(2)	1118 (23)	739 (26)	565 (49)	300 (194)	393 (190)	567 (225)	50 (159)	-31 (176)	27 (166)
C(3)	1200	-3000	8200	1600 (U)					
C(4)	4097 (35)	346 (34)	1839 (68)	879 (323)	569 (251)	1084 (335)	-285 (226)	237 (264)	160 (230)
C(5)	3935 (32)	-2025 (31)	2288 (69)	670 (270)	454 (236)	1223 (367)	302 (205)	147 (254)	170 (229)
C(6)	351 (49)	-3424 (32)	3902 (66)	2557 (619)	371 (216)	686 (298)	503 (293)	-271 (336)	-337 (203)

Fig. 1. Stereoscopic drawing showing the AgI lattice of Ag₄I₆C₄H₁₂N₂·4C₃H₇NO.

Karle, 1966), with the program *PHASE* from the X-RAY 72 set of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). All other computations were carried out with these programs. A full-matrix least-squares refinement with individual anisotropic thermal factors and unit weights assigned to all reflexions led to an R of 0.066 [$R = \sum(|F_o| - |F_c|) / \sum |F_o|$].* Upon refinement, C(3) had shifted to a position only 1.3 Å from S(1). A difference synthesis showed the electron density in the region between these two atoms to be smeared out. Approximate atomic parameters were assigned to C(3) and kept constant during refinement.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31027 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

Standard deviations are in parentheses.

C(1), N(1) and I(3) are related to C(1'), N(1') and I(3)', respectively, by a centre of symmetry. I(1) and I(3') are related to I(1)' and I(3)'', respectively, by a unit cell translation in the c direction.

Ag(1)–I(1')	2.79 (2)	Ag(2)–I(1)	2.79 (2)
Ag(1)–I(2)	2.82 (2)	Ag(2)–I(2)	2.81 (2)
Ag(1)–I(3)	2.94 (2)	Ag(2)–I(3)	2.93 (2)
Ag(1)–I(3')	2.94 (2)	Ag(2)–I(3')	2.96 (2)
I(1)–I(2)	4.73 (2)	I(2)–I(1')	4.69 (2)
I(1)–I(3)	4.64 (2)	I(2)–I(3')	4.72 (2)
I(1)–I(3')	4.68 (2)	I(3)–I(1')	4.67 (2)
I(2)–I(3)	4.76 (2)	I(3)–I(3')	4.57 (2)
I(2)–I(3')	4.74 (2)	I(3)–I(3'')	4.62 (2)
C(1)–N(1')	1.51 (3)	S(2)–O(2)	1.50 (2)
C(1)–C(2)	1.50 (4)	S(2)–C(4)	1.81 (5)
C(2)–N(1)	1.53 (4)	S(2)–C(5)	1.80 (5)
I(1)–Ag(2)–I(2)	115.1 (2)	I(2)–Ag(1)–I(3)	111.4 (2)
I(1)–Ag(2)–I(3)	108.4 (2)	I(2)–Ag(1)–I(3')	110.0 (2)
I(1)–Ag(2)–I(3')	108.7 (2)	I(2)–Ag(1)–I(1')	113.3 (2)
I(2)–Ag(2)–I(3)	111.9 (2)	I(3)–Ag(1)–I(3')	103.5 (2)
I(2)–Ag(2)–I(3')	110.2 (2)	I(3)–Ag(1)–I(1')	109.0 (2)
I(3)–Ag(2)–I(3')	101.7 (2)	I(1)–Ag(1)–I(3')	109.2 (2)
N(1')–C(1)–C(2)	111.4 (2.5)	O(2)–S(2)–C(4)	105.1 (1.9)
C(1)–C(2)–N(1)	111.9 (2.5)	O(2)–S(2)–C(5)	106.9 (1.6)
C(1')–N(1)–C(2)	111.0 (2.2)	C(4)–S(2)–C(5)	98.8 (2.3)

The scattering factors were those of Cromer & Mann (1968). The final atomic parameters are given in Table 1. Table 2 lists selected interatomic distances and angles.

Discussion. The atomic arrangement of the AgI lattice of $\text{Ag}_4\text{I}_6\text{C}_4\text{H}_{12}\text{N}_2 \cdot 4\text{DMSO}$ and the atomic numbering (*ORTEP*: Johnson, 1965) are shown in Fig. 1. The Ag are tetrahedrally surrounded by I atoms with an average Ag...I distance of 2.87 Å. The tetrahedra are doubly edge-shared, forming a continuous framework which extends in the c direction. All the tetrahedral holes thus created are occupied by Ag atoms which line up to form a near linear array in the direction of c . The average Ag...Ag distance is 3.27 Å. The piperazine dihydronium ion is located on the symmetry centre at 0, 0, 0 with only one half of it contributing to the asymmetric unit.

It is of interest to compare the structural features observed in $\text{Ag}_4\text{I}_6\text{C}_4\text{H}_{12}\text{N}_2 \cdot 4\text{C}_2\text{H}_6\text{SO}$ and in $\text{Ag}_{10}\text{I}_{12}\text{C}_4\text{H}_{12}\text{N}_2 \cdot 4\text{C}_3\text{H}_7\text{NO}$ (Coetzer, 1975). The latter contains a three-dimensional network of I tetrahedra with Ag atoms occupying only one fourth of the tetrahedral vacancies. The tetrahedra in $\text{Ag}_{10}\text{I}_{12}\text{C}_4\text{H}_{12}\text{N}_2 \cdot 4\text{C}_3\text{H}_7\text{NO}$ are all face-sharing compared to the edge-sharing of I tetrahedra in $\text{Ag}_4\text{I}_6\text{C}_4\text{H}_{12}\text{N}_2 \cdot 4\text{C}_2\text{H}_6\text{SO}$. The Ag atoms in the latter form linear chains while discrete five-membered rings of Ag atoms are found in the former.

Crystals of $\text{Ag}_4\text{I}_6\text{C}_4\text{H}_{12}\text{N}_2 \cdot 4\text{C}_2\text{H}_6\text{SO}$ are unstable under atmospheric conditions and gradually disintegrate as a result of loss of DMSO.

References

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