Crystal Structure of a 1 : 1 Complex Between Silver Iodide and Morpholine

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Crystals of the 1 : 1 complex between silver iodide and morpholine (AgI,C_4H_9NO) are monoclinic. a = 18.14 ± 0.03, b = 4.528 ± 0.010, c = 9.180 ± 0.020 Å, β = 95.9 ± 0.10, space group $C2$, Z = 4. The structure was solved by use of diffractometer data by the heavy-atom method and refined by full-matrix least-squares to R' 0.048 for 311 independent reflections. The structure has bands of coplanar iodide ions running parallel to the b axis, arranged within the band at the corners of nearly equilateral triangles. The Ag ions are placed alternately above and below successive I_3 triangles. Chair-shaped morpholine molecules are attached to the strings by donation of the nitrogen lone-pair to each silver. Along the strings adjacent morpholine molecules are NH $\cdots$ O bonded to each other.

THE X-ray structure analysis of the 1 : 1 complex between silver iodide and morpholine (AgI,C_4H_9NO) is part of a series being studied [1-4] because of interest in the bonding mechanisms whereby silver iodide and its complexes [5] may act as ice nucleants in supercooled clouds and fogs. The amine complexes are of added interest since minute traces of amines reduce the nucleating ability of silver iodide.[6] Several inorganic silver iodide complexes are solid electrolytes with ionic conductivities approaching those of liquid electrolytes.[7-10] At least two other silver iodide–amine complexes have had high electrical conductivity.[11-13] Conduction mechanisms and applications of such highly conducting materials in solid-state batteries, capacitors, and timing devices have been discussed.[14-16]

EXPERIMENTAL

Small colourless crystals of the complex were prepared by simply dissolving silver iodide in warm morpholine and cooling the solution.

Crystal Data.—AgI,C_4H_9NO, M = 329.9. Monoclinic, a = 18.14 ± 0.03, b = 4.528 ± 0.010, c = 9.180 ± 0.20, β = 95.9° ± 0.1°, U = 750.4 Å^3, D_m = 2.65, Z = 4, D_c = 2.49, $F(000)$ = 592. Space group $C2$, Cm, or $C2/m$ from systematic absences: hkl when $h + k = 2n + 1$, $h0l$ when $h = 2n + 1$, and $0k0$ when $h = 2n + 1$; structure determination confirmed space group $C2$. Mo radiation, $\lambda(K_\alpha)$ = 0.7101, $\lambda(K_{\alpha_1})$ = 0.709 26, $\lambda(K_{\alpha_2})$ = 0.713 54 Å.

The crystals were sealed into capillaries to prevent loss of morpholine. They darkened slightly on repeated exposure to X-rays, but examination of Weissenberg pictures revealed no additional spots or streaking as a result of this.

Intensity data (Mo-K_α) were collected on 0.01° incrementing Datex automated General Electric XRD 5 1/4-circle goniostat equipped with pulse-height selection. The crystal was almost cubic with edges slightly <0.001 cm. All possible total intensities (I_m) were measured for 0° < 2θ < 40°. The moving-crystal, moving-counter, 2θ scan method was used for measuring (I_m) (2θ scan = 3.66° at 2°min^{-1}). Stationary-crystal–stationary-counter background counts of 20 s (B_1 and B_2) were made at each end of each 2θ scan. The integrated intensity (I) was calculated as $I = I_m - 2.745$ ($B_1 + B_2$). Structure factors were obtained by the applica-

[1] G. B. Ansell, L. A. Burkardt, and W. G. Finnegan, *Chem. Comm.*, 1969, 459.

[2] G. B. Ansell and W. G. Finnegan, *Chem. Comm.*, 1969, 960.

[3] G. B. Ansell and W. G. Finnegan, *Chem. Comm.*, 1969, 1300.

[4] G. B. Ansell, *J. Chem. Soc. (B)*, 1971, 443.

[5] L. R. Johnson and B. L. Davis, *J. Appl. Cryst.*, 1972, **5**, 194.

[6] F. K. Odencrantz, *J. Atm. Sci.*, 1968, **25**, 337.

[7] J. N. Bradley and P. D. Greene, *Trans. Faraday Soc.*, 1967, **63**, 424, 2516.

[8] S. Geller, *Science*, 1967, 310.

[9] J. A. A. Ketalaar, *Z. Krist.*, 1934, **87**, 436.

[10] B. Scrosati, *J. Electrochem. Soc.*, 1971, 899.

[11] S. Geller, *Science*, 1972, **170**, 1016.

[12] S. Geller and B. B. Owens, *J. Phys. and Chem. Solids*, 1972, **33**, 1241.

[13] S. Geller and M. D. Lind, *J. Chem. Phys.*, 1970, **52**, 5854.

[14] P. D. Greene, *New Scientist*, 1972, 321.

[15] P. D. Greene, *Electronics and Power*, 1972, 395.

[16] H. Wiedersich and S. Geller, ' The Chemistry of Extended Defects in Non-metallic Solids,' North-Holland, Amsterdam, 1970, p. 629.

tion of the usual Lorentz and polarization corrections. Intensities were not corrected for absorption. Equivalent (hkl) and $(\bar{h}kl)$ intensities were averaged; of 408 averaged intensities obtained, only those with a net count $> 1.5[I_m/(2.745)(B_1 + B_2)]$ were used for preliminary calculations. During refinement seven other reflections were also rejected since they either appeared to require an extinction correction or had abnormal background measurements. 311 Reflections were used in the final least-squares refinement.

Solution and Refinement of the Structure.—The silver and iodide co-ordinates were found by solution of three-dimensional Patterson diagrams. These two atoms refined anisotropically to R 0.106.[17] A difference-Fourier synthesis at this stage revealed the position of atoms within the morpholine rings. Additional isotropic refinement of these parameters reduced R to 0.047. Nine hydrogen atoms were then placed at the computed tetrahedral positions with an isotropic temperature factor 6.0 $Å^{-2}$, but were not refined. Continued anisotropic refinement of silver and iodine and isotropic refinement of nitrogen, carbon, and oxygen was terminated at R 0.045, R' 0.048. During the final cycles of refinement the weighting scheme used was: for $F > 70$, $w = 70/F_0$, and for $F < 70$, $w = F_0/70$, chosen to maintain similar values of mean $w\Delta^2$ for ranges of increasing F_0. It was noted that estimated errors along the b axis are longer than those along a and c. This is obviously a result of correlation between the y parameters of Ag and I but was not sufficiently high to warrant refining them separately, however. Even though the y parameter of Ag is so close to 0.5, no way of placing Ag, I, and the morpholine molecule at the special positions of $C2/m$ seem possible. Final atomic co-ordinates and thermal parameters are given in Table 1, and bond lengths and angles are in Table 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21490 (3 pp.).*

Arrangement of silver and iodide ions and the packing of morpholine around them is illustrated in Figures 1 and 2.[18] Scattering factors for carbon, nitrogen, oxygen, and hydrogen were taken from ref 19; scattering factors corrected for the real part of anomalous dispersion for Ag and I were taken from ref. 20.

RESULTS

Description of the Structure.—The structure has bands of coplanar iodide ions running parallel to the b axis. These ions are arranged within the bands at the corners of nearly equilateral triangles. Silver ions are placed alternately above and below successive I_3 triangles. The structure could also be described as having $(I \cdots I)$ edge-shared (AgI_3) tetrahedra forming strings running parallel to the b axis. Chair-shaped morpholine molecules are attached to the strings by donation of the nitrogen lone-pair to each silver. Adjacent morpholine molecules along a string are NH $\cdots$ O bonded to each other. This outer layer of morpholine molecules separates the strings. Figure 1 and 2 illustrate these structural features.

Within the triangular I_3 base of each (AgI_3) tetrahedra $I(1) \cdots I(1^I)$, $I(1) \cdots I(1^{II})$, $I(1^I) \cdots I(1^{II})$ distances are 4.697, 4.528, and 4.697 Å, with angles at $I(1)$, $I(1^I)$, and

* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

[17] W. R. Busing, K. O. Martin, and H. A. Levy, A Fortran Crystallographic Least Squares Program, Report ORNL TM305, Oak Ridge National Laboratory, Tennessee, 1962, modified by W. C. Hamilton to correct for anomalous dispersion.

$I(1^{II})$ of 61.2, 67.6, and 61.2°. Zig-zag strings of silver ions (one on either side of the string) have Ag $\cdots$ Ag 3.304 Å.

TABLE 1

Atomic fractional co-ordinates ($\times 10^4$) and thermal parameters,* with estimated standard deviations in parentheses

	x	y	z	$B/Å^2$ ($\times 10^2$)
Ag(1)	2 395(1)	4 975(24)	1 273(2)	*
I(1)	3 333(1)	0(0)	1 700(2)	*
C(1)	859(20)	1 509(98)	1 607(39)	512(91)
C(2)	288(14)	598(80)	2 478(28)	244(64)
C(3)	1 007(14)	375(114)	4 631(28)	306(64)
C(4)	1 637(19)	1 706(97)	3 912(39)	431(80)
N(1)	1 414(12)	3 296(58)	2 588(22)	205(45)
O(1)	563(11)	−1 298(49)	3 647(21)	282(42)
H(1) †	682	2 763	641	
H(2)	1 163	−258	1 201	
H(3)	−149	−319	1 816	
H(4)	85	2 610	2 946	
H(5)	691	2 189	4 987	
H(6)	1 198	−857	5 565	
H(7)	2 050	−43	3 654	
H(8)	2 010	3 124	4 657	
H(9)	1 110	5 178	2 897	

* Final anisotropic thermal parameters ($\times 10^4$) in $\beta = h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2(hk\beta_{12} + hl\beta_{13} + kl\beta_{23})$, with parameters:

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag(1)	26(1)	594(18)	122(4)	−32(10)	10(1)	−89(20)
I(1)	22(1)	724(16)	83(2)	52(8)	−1(1)	−42(17)

† All hydrogen atoms have $B = 6.0$ $Å^{-2}$.

TABLE 2

Bond lengths (Å) and angles (°); standard deviations were calculated from the formula given by G.A. Jeffrey and D. W. Cruickshank, *Quart. Rev.*, 1953, **7**, 335

(a) Distances

Ag(1) $\cdots$ Ag(1^I)	3.304	C(1)–C(2)	1.441(49)
Ag(1)–I(1)	2.824(6)	C(2)–O(1)	1.424(36)
Ag(1)–I(1^{II})	2.908(6)	O(1)–C(3)	1.374(41)
Ag(1)–I(1^I)	2.845(6)	C(3)–C(4)	1.504(53)
Ag(1)–N(1)	2.376(24)	C(4)–N(1)	1.435(45)
I(1) $\cdots$ I(1^{II})	4.697(1)	N(1)–C(1)	1.501(45)
I(1) $\cdots$ I(1^I)	4.528(1)	N(1)–O(1^I)	3.103(30)
I(1^{II}) $\cdots$ I(1^I)	4.697(1)		

(b) Angles

N(1)–Ag(1)–I(1)	98.5(6)	C(4)–N(1)–O(1^I)	103.7(19)
N(1)–Ag(1)–I(2)	100.7(6)	O(1^I)–N(1)–Ag(1)	109.3(9)
N(1)–Ag(1)–I(1^I)	130.8(6)	C(1)–N(1)–C(4)	111.2(26)
I(1)–Ag(1)–I(1^{II})	110.1(2)	N(1)–C(1)–C(2)	107.6(29)
I(1)–Ag(1)–I(1^I)	106.0(2)	C(1)–C(2)–O(1)	112.7(26)
I(1^I)–Ag(1)–I(1^{II})	109.5(2)	C(2)–O(1)–C(3)	107.4(24)
C(1)–N(1)–Ag(1)	110.7(19)	O(1)–C(3)–C(4)	110.7(29)
C(4)–N(1)–Ag(1)	115.4(20)	C(3)–C(4)–N(1)	114.3(30)
C(1)–N(1)–O(1^I)	105.9(19)		

Roman numeral superscripts refer to the following equivalent positions: I $-x$, $y + 1$, $-z$; II $\frac{1}{2} - x$, $y + \frac{1}{2}$, $-z$.

The next-nearest values are 4.53 Å. The lone-pair donation from the morpholine nitrogen to the silver is evidenced by (a) the N→Ag value of 2.376 Å, which is similar to the values for the same type of bond in the piperidine [1,4] and piperazine [3] complexes, and (b) the almost tetrahedral angles of 110.7 and 115.4° for C(1)–N(1)→Ag(1) and C(4)–N(1)→Ag(1). The short N(1) $\cdots$ O(1) value of 3.103 Å

[18] C. K. Johnson, ORTEP, Report ORNL 3794, Oak Ridge National Laboratory, Tennessee, 1965.
[19] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.
[20] L. H. Thomas and K. Umeda, *J. Phys. Chem.*, 1957, **26**, 293.

between adjacent morpholine molecules attached to (and on the same side of) the string, plus the $Ag(1) \rightarrow N(1) \cdots O(1)$,
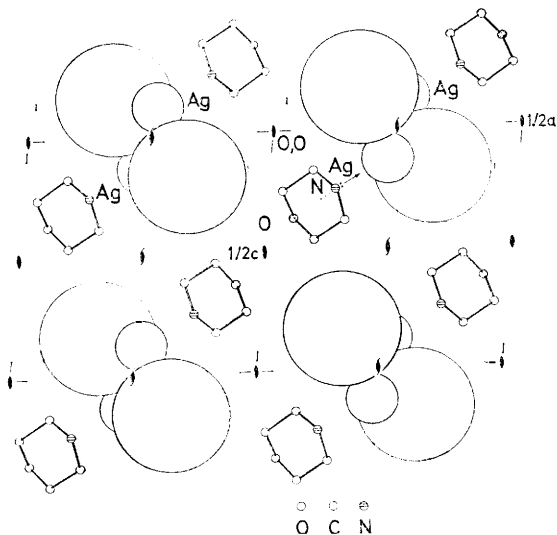

FIGURE 1   The structure viewed down the b axis

$C(1)-N(1) \cdots O(1)^I$, and $C(4)-N(1) \cdots O(1)^I$ angles of 109.3, 105.9, and 103.7° are strong evidence of hydrogen bonding between $N(1)$ and $O(1)$. Within the chair-shaped morpholine ring mean C–C, C–N, and C–O values are 1.47, 1.47, and
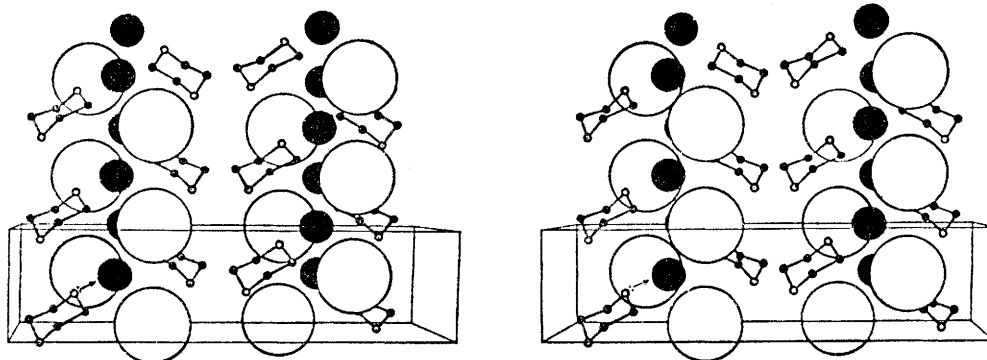
NH_4I,[22] RbI,[22] CsI,[21,23] $[Me_4NI]$.[24] These structures consist of single or double chains of edge-shared iodine regular tetrahedra with an Ag^+ ion at the centre of each tetrahedra. Chain lengths and cationic sites for the accompanying metallic ions usually conform to simple packing and electrostatic requirements. The second group of which $[(C_5H_5NH)Ag_5I_6]$,[11,12] $[(Me_4N)Ag_{13}I_{15}]$,[13] $[RbAg_4I_5]$,[7,8] and $[Ag_2HgI_4]$[9] are examples, having uniquely high electrical conductivities. This is attributed to free movement of silver ions within channels formed by edge- and face-sharing of irregular iodine tetrahedra and octahedra; AgI also has a high electrical conductivity. The third group consists of structures having sets of silver ions (often pairs) at sites on iodine polyhedra forming (Ag/I) clusters. In the complex with piperidine [1,4] tetrahedral I_4 clusters have four silver ions set in the tetrahedral faces with $Ag \cdots Ag$ separations of only 2.98—3.09 Å. $[(Et_3As)_4Ag_4I_4]$[26] is similar. Short $Ag \cdots Ag$ separations (2.94—3.13 Å) are also found in $[(C_4H_9)_4NAg_3I_4]$,[25] which has edge-shared I_4 tetrahedra, and the complex with piperazine, where layers of iodide ions exist. In the present morpholine complex the $Ag \cdots Ag$ separations are larger (3.304 Å) and uniform along the band of iodine ions. This suggests there is no significant interaction between silver ions. The complex linear set of co-ordination sites extending along the iodine band do

FIGURE 2   A stereoscopic view of the structure viewed down the c axis and then rotated 5° about a. For clarity, I is shown with a radius of 1.1, Ag with 0.5, and remaining non-hydrogen atoms with 0.1 Å

1.40 Å. These are all a little shorter than accepted paraffinic single-bond values.[19]

DISCUSSION

There appear to be three major categories of silver iodide complexes: (a) those with an accompanying halide, which do not have high electrical conductivity,[21-24] (b) those with accompanying halides which are highly electrically conductive,[7-13] and (c) those with amines or molecules able to donate lone-pairs to the silver. These do not have high electrical conductivity and often have pairs of silver ions at co-ordination sites on iodine polyhedra.[1-4,25,26]

Examples of the first group are complexes with KI,[22]

appear to be unique, however. In all the complexes in this third group it would appear that the presence of a donated lone-pair to the silver provides an environment for large co-ordination sites to be occupied by several silver ions on a variety of iodide packing arrangements. The Ag–I values ranging from 2.824 to 2.908 Å in this compound are similar to values found in all the compounds discussed earlier. No particular significance is attached to the bond values found in the morpholine ring since the estimated standard deviations of these values are quite large.

[21] C. Brink and C. H. MacGillavry, Acta Cryst., 1949, 2, 158.
[22] C. Brink and H. A. Kroese, Acta Cryst., 1952, 5, 433.
[23] C. Brink, N. F. Binnendijk, and J. A. Van de Linde, Acta Cryst., 1954, 7, 176.
[24] Vons Hans-Jurgen Mayer, Acta Cryst., 1963, 16, 788.
[25] C. J. Gilmore, P. A. Tucker, S. F. Watkins, and P. Woodward, J. Chem. Soc. (A), 1971, 1337.
[26] A. F. Wells, Z. Krist., 1936, 94, 447.