The Crystal Structure of a Complex Between Silver Iodide and Morpholine (AgI,C_4H_9NO)

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Summary An X-ray analysis of the structure of the complex between silver iodide and morpholine has been carried out.

THE detailed structure determination of the complex between silver iodide and morpholine (AgI,C_4H_9NO) is the second in a series of such determinations[1] to establish the role of silver iodide and related compounds when they act as ice nuclei in supercooled clouds and fogs.

The colourless needle shaped crystals of the complex were prepared in the same way as the ($AgI,C_5H_{11}N$) complex.[1] They are monoclinic, $a = 18{\cdot}14$, $b = 4{\cdot}53$, $c = 9{\cdot}18$ Å, $\beta = 95{\cdot}9°$, $Z = 4$, $D_m = 2{\cdot}65$ g. cm.$^{-3}$, $D_c = 2{\cdot}81$ g. cm.$^{-3}$. Systematic absences of X-ray reflections (hkl, $h + k = 2n + 1$; $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$) and the subsequent structure determination have shown the space group to be $C2$.

The structure determination was based on 406 independent observed reflections measured by the moving-crystal moving-counter method on a single crystal orienter using Zr-filtered Mo radiation.

Silver and iodide positions were found by interpretation of a Patterson projection and packing considerations. The morpholine ring was found with a difference Fourier when $R = 0{\cdot}14$. The introduction of the six ring atoms into the full-matrix structure-factor calculations immediately lowered the R value to 0·10. Subsequent positional and anisotropic refinement for silver and iodine and positional and isotropic refinement for carbon, nitrogen, and oxygen lowered the unweighted R value to 0·068. A difference Fourier at this stage revealed no extraneous features. Corrections for absorption and anomalous scattering have not been applied yet.

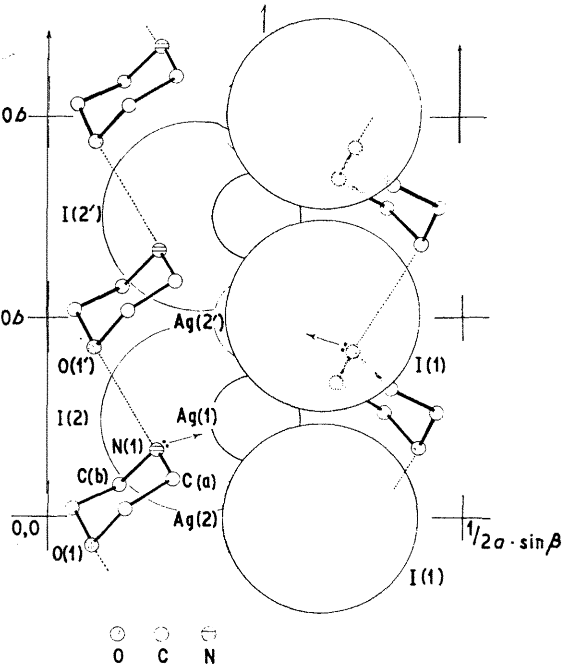

FIGURE 1. *The complex as seen looking down the* c-*axis.* Ag(1)–I(1) = 2·80, Ag(1)–I(1′) = 2·86, Ag(1)–I(2) = 2·90, I(1)–I(1′) = 4·53, I(1)–I(2) = 4·68 and Ag(1)–Ag(2′) = 3·30 Å. (σ = 0·01 Å *for these bond lengths*).

The structure consists of zig-zag strings of iodide ions lying parallel to the *b*-axis with silver ions embedded into them (Figure 1). These strings of ions are separated by morpholine molecules (Figure 2) which are themselves attached to the strings by donation of a lone-pair of electrons from nitrogen to silver. It also appears as if adjacent morpholine molecules attached to the same $(AgI)_n$ strings are hydrogen-bonded to each other, with the hydrogen attached to the nitrogen in one molecule forming a hydrogen-bond with the oxygen in the adjacent molecule (Figure 1). Evidence for the suggested structure is:

(a) The C(a)–N(1)–Ag(1) and C(b)–N(1)–Ag(1) angles in Figures 1 and 2 are both 110°.

(b) The Ag(1)–N(1) distance in Figures 1 and 2 is 2·39 ($\sigma = 0{\cdot}04$) Å. This is a little larger than the value of 2·34 ($\sigma = 0{\cdot}03$) Å found for similar bond in the $AgI,C_5H_{11}N$ complex[1] where in this case, though, a much weaker type of hydrogen-bond was suggested for the hydrogen attached to nitrogen. It is, however, considerably shorter than the value of 2·561 Å in AgN_3[2] where the Ag–N bond is considered to be 1/4 order.

(c) The N(1)–O(1′) distance (Figure 2) is 2·98 ($\sigma = 0{\cdot}05$) Å; a value short enough to suggest hydrogen-bonding[3] since it is at least 0·3 Å less than might be expected from the van der Waals separation between N–H and oxygen.[4]

(d) The O(1′)–N(1)–C(a), O(1′)–N(1)–C(b), and O(1′)–N(1)–Ag(1) angles are 110°, 110°, and 111° respectively, suggesting that if the lone-pair, hydrogen, C(a), and C(b) are arranged tetrahedrally around N(1), then the suggested N–H · · · · O bond lies almost along the N(1)–O(1′) direction.

The morpholine ring is chair-shaped.

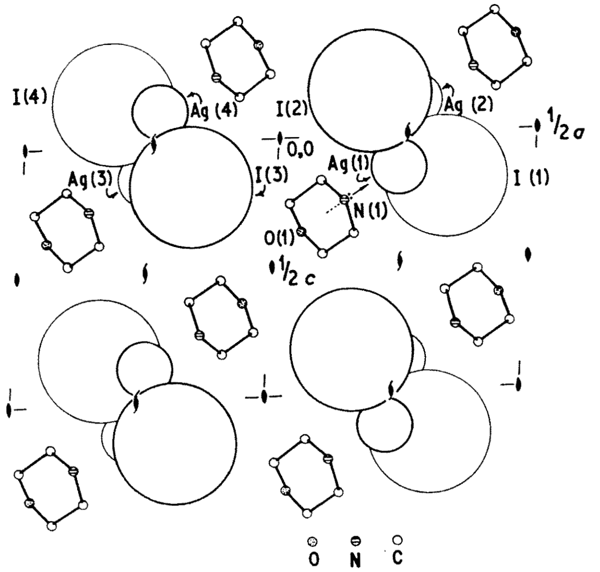

FIGURE 2. *The contents of the unit cell as shown in projection down the* b-*axis.*

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

[2] E. W. Hughes, personal communication.

[3] "The International Tables for *X*-Ray Crystallography," Kynoch Press, Birmingham, 1962, vol. 3, p. 273.

[4] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1960.