The Structure of a Complex between Silver Iodide and Piperidine ($AgI,C_5H_{11}N$)

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

DETAILED structure analysis of the complex between silver iodide and piperidine ($AgI,C_5H_{11}N$) has been undertaken.

Colourless crystals of the complex suitable for *X*-ray investigation were prepared by warming silver iodide with sufficient piperidine to dissolve the silver iodide and allowing the resulting solution to cool. The crystals are orthorhombic; $a = 20{\cdot}220$, $b = 8{\cdot}226$, $c = 10{\cdot}240$ Å, $Z = 8$, $D_m = 2{\cdot}40$ g.cm.$^{-3}$ (water displacement), $D_c = 2{\cdot}49$ g.cm.$^{-3}$, space group *Pcna* from the systematic absences.

It was necessary to seal the crystals in capillaries to prevent loss of piperidine during *X*-ray examination. The crystals darkened upon exposure to *X*-rays, but examination of repeated exposures revealed no additional spots or streaking, and hence darkening was assumed to be due to slow decomposition of the material.

556 Independent observed reflections were measured by the moving-crystal moving-counter method on a single-crystal orienter using Zr-filtered Mo-radiation. The silver and iodine positions were found by interpretation of the Harker sections $u = 0$ and $w = 0$. They were refined by full-matrix anisotropic least-squares to R value 0·135. A difference Fourier at this stage clearly revealed all the carbon and nitrogen atoms of the piperidine ring. The introduction of these atoms into the analysis lowered R to 0·091, and at the present state of anisotropic refinement for silver and iodine and isotropic for carbon and nitrogen R is 0·059. Corrections for absorption and anomalous dispersion have not yet been applied.

As a first approximation, the structure may be regarded as consisting of layers in the order piperidine–iodide–silver–iodide–piperidine–stacked along the *b*-axis. The silver iodide occurs as tetrahedral clusters of iodide ions with silver embedded in the faces of the tetrahedron (Figure 1). Figure 2 shows adjacent $(AgI)_4$ tetrahedra in the *b* direction are held together by the piperidine molecule, the nitrogen of each piperidine molecule donating a lone-pair to a silver in one tetrahedron, and the hydrogen attached to the nitrogen forming a weak hydrogen bond with an iodine in the tetrahedron above or below. Evidence for the suggested structure:

(*a*) The C(1)–N–Ag and C(5)–N–Ag angles (Figure 2) are 115° and 114° respectively. (*b*) The Ag–N distance (Figure 2) is 2·34(3) Å. This is somewhat larger than the value of 2·22 Å found in AgCNS[1] where it is suggested that silver is covalently bonded to both sulphur and nitrogen in chains N–C–S–Ag–N–. It is, however, considerably shorter than the value of 2·561 Å found in AgN_3[2] where the Ag–N bonding is considered to be 1/4 order. (*c*) The Ag–N–I, C(5)–N–I, and C(1)–N–I angles (Figure 2) are 129·5, 94, and 87° respectively. (*d*) The N–I distance (Figure 2) is 3·82(3) Å. By assuming that the N–H bond may deviate by as much as 15° towards silver (Figure 2) from the line joining nitrogen and iodine it is easy to show that the N–I separation is about 0·5 Å less than might be expected from the van der Waals separation between N and I^-.[3]

The piperidine rings are chair shaped.

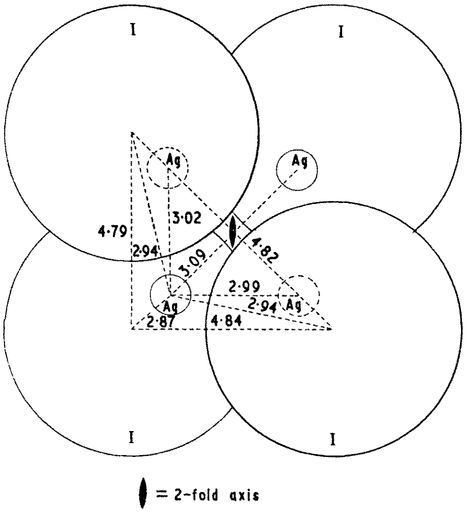

FIGURE 1. *A tetrahedral silver and iodine cluster viewed down the* b-*axis. The silver atoms are at heights* ± 1·033 Å; *iodines at* ±1·702 Å (σ *of bond lengths* = 0·005 Å).

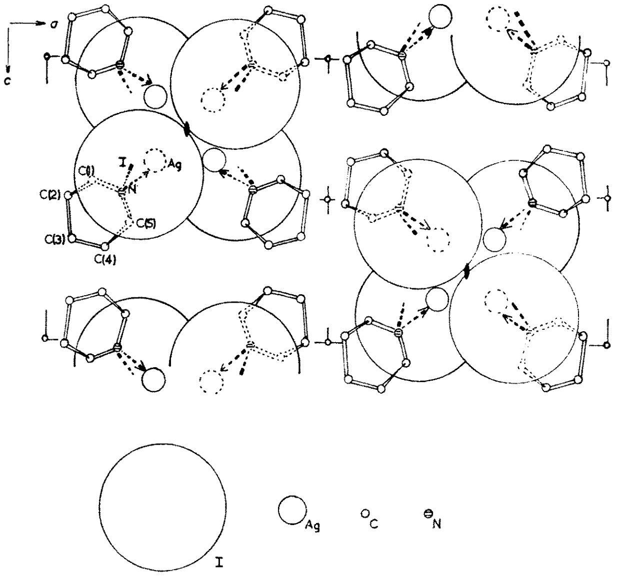

FIGURE 2. *A view of the Ag–piperidine complex viewed down the* b-*axis. The silver atoms at* 1·033 *and* 7·233 Å *occur in different tetrahedra.*

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[1] I. Lindqvist, *Acta Cryst.*, 1957, **10**, 29.

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

[3] L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, 1960.