Silver Ion–Bullvalene Complex Formation resulting in an Infinite Helical Structure with Ag^+–H_2O Co-ordination

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WHILE attempting to prepare a sample of the 2 : 1 bullvalene–silver tetrafluoroborate complex[1,2] suitable for single crystal *X*-ray studies, we succeeded in isolating a few crystals of a 1 : 1 bullvalene–$AgBF_4$ monohydrate ($C_{10}H_{10}$,$AgBF_4$,H_2O). The structure of this complex has been elucidated as part of a series of structural studies on bullvalene and its derivatives.[2]

The transparent needles, from propan-2-ol, belong to the monoclinic system with $a = 8{\cdot}49 \pm 0{\cdot}02$, $b = 14{\cdot}84 \pm 0{\cdot}03$, $c = 18{\cdot}74 \pm 0{\cdot}04$ Å, and $\beta = 107°40' \pm 20'$ (Mo-K_α, $\lambda = 0{\cdot}7107$ Å). The space group is $P2_1/c$. The density ($D_m = 1{\cdot}95$ g.cm.$^{-3}$) indicates that the unit cell contains eight $C_{10}H_{10}$,$AgBF_4$,H_2O species ($D_c = 2{\cdot}02$), two of which must be crystallographically independent. A total of 2164 independent structure amplitudes was obtained from visual estimates of equi-inclination Weissenberg photographs (Cu-K_α radiation). The structure was determined by the heavy-atom method and refined by full-matrix least-squares methods, incorporating anisotropic temperature factors, to give an *R*-factor of 0·12 on all observed reflexions. The structure viewed along the *a* and *b*-axes is illustrated in Figures 1 and 2.

Each Ag^+ ion complexes to two bullvalene molecules, and each bullvalene molecule is complexed by two Ag^+ ions. The resulting structure is an irregular spiral or helix around the 2_1 screw axis. Another co-ordination position of each silver ion, directed outward from the axis of the helix, is occupied by a water molecule which, in turn, engages in hydrogen bonding with the tetrafluoroborate anions. The shortest $Ag^+ \cdots F$ contact is 2·94 Å. The two $Ag^+ \cdots O$ distances are 2·32 and 2·42 Å, in close agreement with the $Ag^+ \cdots O$ distances found in various silver nitrate–olefin complexes.[3–5]

Each Ag^+ ion forms one short and one long Ag^+–olefin contact with both complexing bullvalene molecules. The four short $Ag^+ \cdots C{=}C$ midpoint distances are 2·36, 2·37, 2·42, and 2·46 Å, while the four long contacts are 2·96, 2·97, 3·10, and 3·19 Å. Similar ranges of Ag^+–olefin distances were found in the 3 : 1 bullvalene–$AgBF_4$ complex[2,6] When the individual $Ag^+ \cdots C$

distances are considered, further evidence is obtained for the unsymmetrical Ag$^+$–olefin complexing pattern discussed elsewhere.[2] All the double bonds in the crystal either form *one* short Ag$^+$ contact or *two* long Ag$^+$ contacts (such as occur in the cyclooctatetraene–$AgNO_3$ complex[4]).

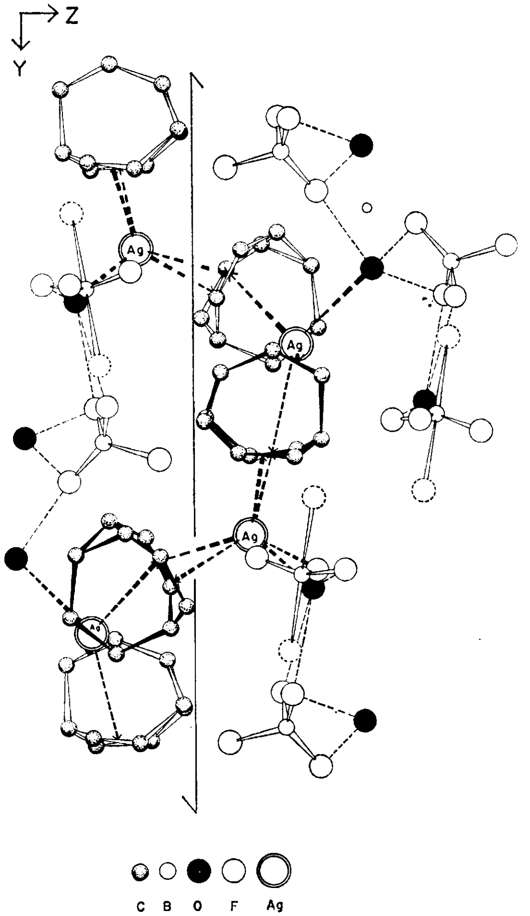

FIGURE 1. *The structure viewed along the* a-*axis.* Ag$^+ \cdots$C$=$C *(mid-point) and Ag$^+ \cdots$O contacts are shown by dark, discontinuous lines, while the hydrogen bonds between water and the* BF_4^- *anions are shown by single, discontinuous lines. The two positions for the apical fluorine atom in the disordered* BF_4^- *anion are shown by discontinuous circles.*

The C–C distances (avg. e.s.d. ± 0·04 Å) do not indicate that valence tautomerism is taking place in the crystal, and support the conclusion that strong Ag$^+$ complex formation (*i.e.*, as inferred from short distances) to two double bonds in bullvalene is sufficient to "freeze" any rearrangement.[2]

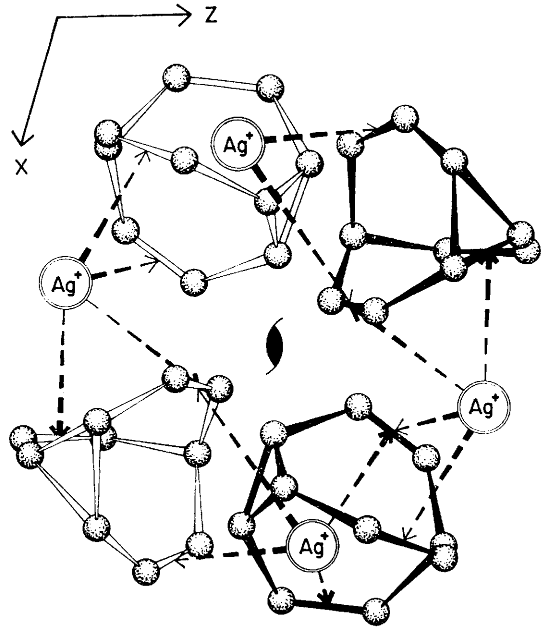

FIGURE 2. *A view of the silver–bullvalene arrangement looking down the* b *(helical)-axis. The water molecules and* BF_4^- *anions are not shown.*

One of the tetrafluoroborate anions appears to crystallize in a two-fold disordered fashion, with three of the fluorine atoms occupying the same positions in all unit cells but the boron and fourth fluorine atoms occupying two different positions on a statistical basis. The other BF_4^- anion appears to be fully ordered.

This work was supported in part by grants from the U.S. Public Health Department.

(*Received, November* 6*th*, 1967; *Com.* 1199.)

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