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The Crystal and Molecular Structure of a Silver–Bullvalene Complex[1,2]

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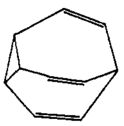
Abstract: A three-dimensional X-ray structure analysis has been carried out on a (3:1) bullvalene–silver fluoroborate complex. The crystals are monoclinic, with $a = 12.44$, $b = 10.18$, $c = 19.47$ A, and $\beta = 95° 40'$. There are four molecules of $(C_{10}H_{10})_3 \cdot AgBF_4$ in the space group $P2_1/c$. The analysis was based on film data collected at 4° on three separate crystals, as the crystals decompose upon exposure to X-rays and light over a period of 4–5 days. The final R factor on 1734 reflections is 0.12. The structure consists of discrete $(C_{10}H_{10})_3 \cdot Ag^+$ cations and BF_4^- anions. The mode of complex formation of Ag^+ to one of the bullvalene molecules differs from that to the other two. The former case is unusual in that silver interacts almost equally with two double bonds in the one molecule. An explanation is offered for the asymmetric disposition of silver with respect to the two carbon atoms forming the double bond involved in complex formation. There is evidence that two of the bullvalene molecules may undergo a reduced degree of valence tautomerism in the crystal.

Investigations on reversible degenerate Cope rearrangements led Doering and Roth to consider the unique properties to be expected of the then hypothetical tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene (I), or "bullvalene" as it became known.[4] Doering and Roth postulated that the self-interconversion of bullvalene should be greater than the simpler bicyclo[5.1.0]octa-2,5-diene (II), due to "locking" of the 3,4-homotropilidene fragment in bullvalene in a *cisoid* configuration, deemed necessary for the Cope rearrangement, and also due to different 3,4-homotropilidene fragments in bullvalene which might offer the possibility of rearrangement. Under conditions where the rate of self-rearrangement of bullvalene is rapid compared to the nmr relaxation time, they predicted that the four chemically nonequivalent sets of protons would be magnetically indistinguishable.[4] Shortly thereafter, Schröder[5] succeeded in synthesizing bullvalene and fully confirmed these predictions. While the infrared spectrum was independent of temperature, vinyl and aliphatic protons could be clearly distinguished in the nmr spectrum at −85°, but at 15° the distinction faded, and at 120° the nmr showed a sharp singlet whose chemical shift could be accounted for in terms of an averaging of the individual shifts at the lower temperatures. Doering and Roth[6] were careful to emphasize that the phenomenon should be described as tautomerism rather than resonance, and the name "valence tautomer" or "fluctional structure" has been used for a single form of a molecule undergoing rapid self-rearrangement. Saunders[7] measured the rate of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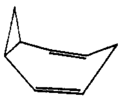
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(1) This work was supported in part by the National Institutes of Health (GM 12470-02 and 5Tl GM 722-05).

(2) Preliminary communication: M. G. Newton and I. C. Paul, *J. Am. Chem. Soc.*, **88**, 3161 (1966).

(3) Author to whom correspondence concerning this investigation should be addressed.

(4) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(5) G. Schröder, *Angew. Chem.*, **75**, 722 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 481 (1963).

(6) W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963).

self-rearrangement of bullvalene from a line-shape analysis of the nmr data, and Allerhand and Gutowsky[8] measured the rate by spin-echo nmr techniques and also extended their investigations to determine the rates of rearrangement of Ag^+–bullvalene complexes in various solutions. They found that although the rearrangement was slower in these complexes, it was not completely eliminated. In the course of this work, Allerhand and Gutowsky isolated several solid complexes, and we became interested in examining these compounds crystallographically to determine whether the bullvalene molecules crystallize in an ordered fashion and, if so, to determine details of bonding and geometry. The nature of fluctional structures in the crystal and the comparison of properties of valence tautomers in solution and in the crystal have been matters of considerable recent interest in relation to the cyclooctatetraene–metal carbonyls.[9–13]

Unfortunately, all of the solids isolated by Allerhand and Gutowsky either proved to be highly disordered, conceivably providing evidence for the occurrence of valence tautomerism in the solid state, or decomposed rapidly upon exposure to light or X-rays. We found, however, that after the reported bullvalene–$AgBF_4$ (2:1) complex[8] had been left for several months and had partially decomposed leaving an unidentified deposit, it could be recrystallized from isopropyl alcohol to give well-formed white laths of a bullvalene–$AgBF_4$ (3:1) complex, which was moderately stable to X-rays and light, and gave X-ray spectra with sin θ up to 0.75. A single crystal X-ray analysis of this complex is described.

Experimental Section

(i) **Preparation of Compounds.** The $(C_{10}H_{10})_2 \cdot AgBF_4$ complex (0.15 g), described by Allerhand and Gutowsky[8] and which had been stored as a solid at 4° in the absence of light for approximately 6 months, was dissolved by heating in 15 ml of isopropyl alcohol. Crystals formed upon cooling and a metallic lustrous film was deposited on the inside of the glass container. The crystals darken at 130° and the mass completely blackened at 155°, where decomposition appeared complete.

Anal. Calcd for $(C_{10}H_{10})_3 \cdot AgBF_4$: C, 61.5; H, 5.13. Found: C, 61.28; H, 5.25.

After completion of the structural study, we received a sample of bullvalene from Dr. Gerhard Schröder of the Technische Hochschule, Karlsruhe, Germany. By following the procedure of Allerhand and Gutowsky,[8] we were able to isolate a 2:1 complex in microcrystalline form. Recrystallization from isopropyl alcohol yielded some large needle-like crystals embedded among the microcrystals. A second recrystallization from a larger volume of isopropyl alcohol gave a good crop of needles which on analysis were shown to be the 3:1 complex.

Examples of changes in composition of Ag^+–olefin complexes upon recrystallization have been documented.[14,15] The 3:1 complex was found to be much more stable to light than the 2:1 complex.

Anal. Calcd for $(C_{10}H_{10})_2 \cdot AgBF_4$: C, 52.78; H, 4.43. Found: C, 52.46; H, 4.63. Calcd for $(C_{10}H_{10})_3 \cdot AgBF_4$: C, 61.54; H, 5.13. Found: C, 61.39; H, 5.03.

Infrared Spectra. The infrared spectra were recorded as Nujol mulls on NaCl plates at 25° with a Perkin-Elmer 521 grating infrared spectrophotometer.

(ii) **Crystallography.** All photographs were taken in a room at 4° (±1°), and unnecessary exposure of the crystals to light was avoided. The crystals were laths, with an approximate equidimensional cross-section and elongated along the b axis. Cell data were obtained from precession photographs, using Mo $K\alpha$ radiation (λ 0.7107 A). The cell data for $(C_{10}H_{10})_3 \cdot AgBF_4$ ($M = 585.2$) are: monoclinic, $a = 12.44 \pm 0.02$, $b = 10.18 \pm 0.02$, $c = 19.47 \pm 0.03$ A; $\beta = 95° 40' \pm 10'$; $V = 2453.7 \times 10^{-24}$ cm^3; $\rho_{\text{measd}} = 1.54$ g cm^{-3}; $Z = 4$; $\rho_{\text{calcd}} = 1.585$ g cm^{-3}. Linear absorption coefficient, μ (Cu $K\alpha$) = 71.5 cm^{-1}; absent spectra, $h0l$, when $l = 2n + 1$, $0k0$, when $k = 2n + 1$; space group $P2_1/c$ ($C_{2h}{}^5$).

The reflection data were recorded on equiinclination Weissenberg photographs employing Cu $K\alpha$ radiation (λ 1.5418 A). After 4–5 days of X-ray and light exposure, the crystals began to darken noticeably and the intensity of the diffraction spots decreased. This effect appeared to be the result of gradual breakup of the lattice. We looked for, but did not detect, relative changes of intensities within the initial 4–5-day period. The decomposition of the crystals made it impossible for us to record all the data from one specimen. Three crystals, all mounted about the b crystallographic axis, were used to accumulate the data. For each level, Weissenberg photographs were taken on two different crystals during the initial 4–5-day period, and in no instance were any relative intensity differences observed. Intensities for the levels $h0l$ and $h2l$ were measured from the first specimen, the levels $h4l$ and $h5l$ from a second, and the levels $h1l$, $h3l$, $h6l$, and $h7l$ from a third crystal. Initially, the reciprocal lattice levels hnl were placed on a relative scale from $0kl$ and $hk0$ precession photographs. No corrections for absorption were applied. The data fade out completely beyond sin $\theta/\lambda = 0.50$. Of the approximately 2700 recordable reflections within this range, 1734 were observed.

Structure Determination. Initially, we were uncertain as to the exact nature of the complex and consequently the number of molecules in the unit cell. The initial measured density[16] supported a total formula weight of approximately 742 in the asymmetric unit, which could not be rationalized in terms of either a 2:1 or 3:1 complex. The three-dimensional Patterson map, however, could be readily interpreted in terms of a single Ag^+ ion in the asymmetric unit. An electron density map, computed on the signs calculated for the Ag^+ ion contribution, clearly revealed two bullvalene molecules (I and II in Figure 1) grouped around the Ag^+ ion, while a third bullvalene molecule (III in Figure 1) and the tetrafluoroborate anion could be discerned in general outline. This map convinced us that we were examining a 3:1 complex. Inclusion of the 20 carbon atoms and the Ag^+ ion in a structure factor calculation and subsequent computation of a Fourier synthesis provided positions for the carbon atoms of the third bullvalene molecule and approximate positions for the boron and fluorine atoms of the tetrafluoroborate anion. It proved difficult to determine the exact coordinates of the individual atoms in the anion, because of a smearing out of the electron density in this region of the unit cell. Assuming a tetrahedral structure for the ion, geometrically reasonable positions were deduced for the boron and the fluorine atoms. Two cycles of full-matrix least-squares refinement,[17] varying the over-all scale factor and positional and iso-

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(15) J. G. Traynham, *J. Org. Chem.*, **26**, 4694 (1961).

(16) Although only a few single crystals were available to us, we attempted to measure the density of the complex in a number of organic solvents before initiation of the structure analysis. A mixture of iodobenzene and bromoform, in which the crystals were suspended at equilibrium, had a density of 2.01 g cm^{-3}. We have since discovered that the crystals slowly underwent decomposition in mixtures of iodobenzene with either bromoform or carbon tetrachloride leaving a dark residue which was very dense and presumably contained a high proportion of silver. With pure iodobenzene, the crystals floated at the surface, indicating that the density is less than 1.838 g cm^{-3}. The measured value of 2.01 g cm^{-3} was almost certainly a better indication of the density of the decomposition product than that of the pure complex. After preparation of additional $(C_{10}H_{10})_3 \cdot AgBF_4$, we were able to determine the density of the complex reasonably accurately by flotation in an aqueous solution of zinc chloride.

(17) We used an amended version of the program by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, "I. U. C. World List of Crystallographic Computer Programs," 1962, No. 384, International Union of Crystallography.

tropic thermal parameters on the Ag, C, B, and F atoms, were carried out. The quantity minimized was $\Sigma w|F_o - F_c|^2$, and all reflections were given unit weight. Prior to beginning anisotropic refinement, the scale factors among the various *hnl* levels of data were adjusted to give the best fit to the calculated structure factors. These scale factors were not varied during the later stages of refinement, as simultaneous refinement of scale factors and anisotropic temperature parameters is not justified on data collected about a single crystal axis using Weissenberg methods.[18] After two cycles of least-squares analysis, in which the thermal motion of the silver ion was treated anisotropically, there was still considerable distortion in the tetrafluoroborate anion, particularly involving F(3), the fluorine atom nearest silver. Attempts to describe the tetrafluoroborate ion in terms of a partially disordered structure[19] did not afford a satisfactory basis for further progress. After choosing a more chemically acceptable position for F(3), two cycles of anisotropic refinement on the silver, boron, and four fluorine atoms, with all other atoms isotropic, gave much more reasonable dimensions for the anion. No attempt was made to locate or to include hydrogen atoms in any calculations. At the conclusion of the refinement, the shifts in the parameters were much smaller than the estimated standard deviations. The crystallographic *R* factor, defined as $R = \Sigma \, ||F_o| - |F_c|| / \Sigma|F_o|$, was 0.12 for the 1734 observed reflections. The atomic coordinates and temperature factors used in the final calculation are listed in Tables I and II, respectively, and the atom numbering is indicated in Figure 1. The final list of *h*, *k*, *l*, F_o, and F_c values is deposited with the ADI Auxiliary Publications Project.[20]

Table I. Final Atomic Coordinates[a]

	x	*y*	*z*
Ag	0.2300 (1)	0.1050 (2)	0.2071 (1)
B	0.228 (2)	0.627 (4)	0.163 (2)
F(1)	0.322 (2)	0.632 (3)	0.137 (1)
F(2)	0.147 (2)	0.612 (3)	0.114 (1)
F(3)	0.218 (2)	0.740 (2)	0.198 (1)
F(4)	0.237 (2)	0.537 (3)	0.205 (2)
C(1)	0.073 (2)	0.280 (3)	0.088 (1)
C(2)	0.071 (2)	0.285 (3)	0.162 (1)
C(3)	0.028 (2)	0.192 (3)	0.202 (1)
C(4)	−0.027 (2)	0.070 (3)	0.173 (1)
C(5)	0.055 (2)	−0.011 (2)	0.141 (1)
C(6)	0.100 (2)	0.025 (3)	0.086 (1)
C(7)	0.084 (2)	0.152 (3)	0.048 (1)
C(8)	−0.023 (2)	0.221 (3)	0.042 (1)
C(9)	−0.122 (2)	0.172 (3)	0.069 (1)
C(10)	−0.126 (2)	0.109 (3)	0.126 (1)
C(11)	0.362 (2)	0.210 (3)	0.073 (2)
C(12)	0.351 (2)	0.257 (3)	0.142 (1)
C(13)	0.408 (2)	0.202 (3)	0.199 (1)
C(14)	0.495 (2)	0.079 (3)	0.197 (1)
C(15)	0.437 (2)	−0.038 (3)	0.158 (1)
C(16)	0.383 (2)	−0.034 (3)	0.096 (1)
C(17)	0.373 (2)	0.080 (3)	0.047 (1)
C(18)	0.475 (2)	0.172 (3)	0.045 (1)
C(19)	0.570 (2)	0.170 (3)	0.093 (1)
C(20)	0.580 (2)	0.128 (3)	0.156 (1)
C(21)	0.387 (3)	0.011 (4)	0.346 (2)
C(22)	0.290 (2)	−0.034 (3)	0.308 (1)
C(23)	0.188 (2)	−0.020 (3)	0.314 (1)
C(24)	0.143 (2)	0.092 (3)	0.372 (2)
C(25)	0.204 (2)	0.231 (3)	0.368 (1)
C(26)	0.311 (2)	0.238 (3)	0.368 (1)
C(27)	0.395 (2)	0.138 (3)	0.381 (1)
C(28)	0.375 (3)	0.021 (3)	0.436 (2)
C(29)	0.280 (3)	0.001 (3)	0.465 (2)
C(30)	0.180 (2)	0.030 (3)	0.442 (2)

[a] In fractions of the unit cell edge, with the estimated standard deviations (×10^4 for Ag, ×10^3 for other atoms) in parentheses. Origin as in "International Tables for X-Ray Crystallography."

Table II. Final Thermal Parameters[a]

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ag	77 (1)	145 (3)	39 (1)	−21 (4)	12 (4)	56 (1) × 10^4
B	6 (2)	5 (5)	6 (2)	−1 (5)	−3 (3)	9 (4) × 10^3
F(1)	22 (3)	44 (6)	14 (2)	13 (7)	21 (4)	14 (5) × 10^3
F(2)	25 (3)	32 (5)	12 (1)	−5 (6)	−14 (4)	8 (4) × 10^3
F(3)	33 (4)	25 (4)	8 (1)	−27 (6)	6 (3)	0 (3) × 10^3
F(4)	22 (3)	23 (5)	18 (2)	17 (6)	3 (4)	−7 (5) × 10^3

	B_θ		B_θ
C(1)	5.8 ± 0.6	C(16)	5.6 ± 0.6
C(2)	4.7 ± 0.5	C(17)	5.8 ± 0.6
C(3)	4.8 ± 0.5	C(18)	6.9 ± 0.7
C(4)	4.9 ± 0.5	C(19)	6.0 ± 0.6
C(5)	4.3 ± 0.5	C(20)	5.4 ± 0.6
C(6)	5.0 ± 0.6	C(21)	9.7 ± 1.0
C(7)	5.2 ± 0.6	C(22)	6.4 ± 0.7
C(8)	5.9 ± 0.6	C(23)	4.9 ± 0.5
C(9)	5.8 ± 0.6	C(24)	7.7 ± 0.8
C(10)	4.7 ± 0.5	C(25)	6.7 ± 0.7
C(11)	7.4 ± 0.8	C(26)	6.8 ± 0.7
C(12)	6.6 ± 0.7	C(27)	7.3 ± 0.8
C(13)	6.3 ± 0.7	C(28)	8.3 ± 0.9
C(14)	6.6 ± 0.7	C(29)	7.2 ± 0.7
C(15)	5.3 ± 0.6	C(30)	7.2 ± 0.7

[a] Anisotropic temperature factors are expressed in the form, $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$, and isotropic parameters are expressed as $\exp(-B_\theta \sin^2 \theta/\lambda^2]$ with B_θ in A^2. Estimated standard deviations are given in parentheses.

The atomic scattering curves used in the analysis were taken from the compilation in "International Tables for X-Ray Crystallography."[21]

Results and Discussion

Bond distances and angles are given in Tables III and IV, respectively. The molecular structure viewed along the *y* and *z* directions is shown in Figures 1 and 2.

The crystal structure consists of discrete Ag$^+$-(bullvalene)$_3$ units with the tetrafluoroborate anions occupying positions above and below the Ag$^+$ ion (Figure 3). There is no tendency for the Ag$^+$ ion to form continuous chains either through coordination to more than one olefin, as in the crystalline cyclooctatetraene–silver nitrate complex ($C_8H_8 \cdot AgNO_3$),[22] or with the anion through apparent covalent bonds as is found in cyclooctatetraene–silver nitrate,[22] the humulene–silver nitrate adduct ($C_{15}H_{24} \cdot 2AgNO_3$),[23] and in norbornadiene–silver nitrate ($C_7H_8 \cdot 2AgNO_3$).[24] The shortest Ag$^+ \cdots$F distances, above and below the metal ion, are 3.73 and 4.39 A involving F(3) and F(4), respectively. These distances are much greater than the value of 2.62 A for the sum of the ionic radii of Ag$^+$ and F$^-$.[25] The contact distances found in the crystal

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(18) E. C. Lingafelter and J. Donohue, *Acta Cryst.*, **20**, 321 (1966).

(19) Fluoroborate ions have been found to exhibit orientational disorder: *e.g.*, M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Chem. Commun.*, 477 (1965); I. C. Zimmerman, M. Barlow, and J. D. McCullough, *Acta Cryst.*, **16**, 883 (1963).

(20) These are available from American Documentation Institute, Auxiliary Publications Project, Library of Congress, Washington, D. C. 20540, Document No. 9458. A copy may be secured by citing the document number and by remitting $3.75 for photoprints, or $2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(21) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–207.

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(23) J. A. Hartsuck and I. C. Paul, *Chem. Ind.* (London), 977 (1964); A. T. McPhail and G. A. Sim, *J. Chem. Soc., Sect. B*, 112 (1966).

(24) N. C. Baenziger, H. L. Haight, R. Alexander, and J. R. Doyle, *Inorg. Chem.*, **5**, 1399 (1966).

(25) L. Pauling in "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 514.

Table III

Carbon–Carbon Bond Distances (A)

C(1)–C(2)	1.46 ± 0.03	C(11)–C(12)	1.43 ± 0.04	C(21)–C(22)	1.43 ± 0.05
C(1)–C(7)	1.53 ± 0.04	C(11)–C(17)	1.43 ± 0.04	C(21)–C(27)	1.45 ± 0.05
C(1)–C(8)	1.54 ± 0.04	C(11)–C(18)	1.60 ± 0.04	C(21)–C(28)	1.77 ± 0.05
C(2)–C(3)	1.37 ± 0.03	C(12)–C(13)	1.39 ± 0.04	C(22)–C(23)	1.28 ± 0.04
C(3)–C(4)	1.51 ± 0.04	C(13)–C(14)	1.66 ± 0.04	C(23)–C(24)	1.74 ± 0.04
C(4)–C(5)	1.50 ± 0.03	C(14)–C(15)	1.56 ± 0.04	C(24)–C(25)	1.61 ± 0.05
C(4)–C(10)	1.52 ± 0.03	C(14)–C(20)	1.47 ± 0.04	C(24)–C(30)	1.52 ± 0.04
C(5)–C(6)	1.31 ± 0.03	C(15)–C(16)	1.31 ± 0.04	C(25)–C(26)	1.35 ± 0.04
C(6)–C(7)	1.49 ± 0.04	C(16)–C(17)	1.50 ± 0.04	C(26)–C(27)	1.45 ± 0.04
C(7)–C(8)	1.51 ± 0.04	C(17)–C(18)	1.58 ± 0.04	C(27)–C(28)	1.65 ± 0.05
C(8)–C(9)	1.46 ± 0.04	C(18)–C(19)	1.43 ± 0.04	C(28)–C(29)	1.37 ± 0.05
C(9)–C(10)	1.30 ± 0.04	C(19)–C(20)	1.31 ± 0.04	C(29)–C(30)	1.31 ± 0.04

Ag^+–Carbon Distances

Ag···C(2)	2.78 ± 0.02	Ag···C(15)	3.19 ± 0.02
Ag···C(3)	2.66 ± 0.02	Ag···C(16)	3.33 ± 0.03
Ag···C(5)	2.69 ± 0.02	Ag···C(22)	2.48 ± 0.03
Ag···C(6)	2.84 ± 0.03	Ag···C(23)	2.55 ± 0.02
Ag···C(12)	2.58 ± 0.03	Ag···C(25)	3.42 ± 0.03
Ag···C(13)	2.45 ± 0.03	Ag···C(26)	3.46 ± 0.03

Distances in the Tetrafluoroborate Anion

B–F(1)	1.32 ± 0.04	B–F(3)	1.34 ± 0.05
B–F(2)	1.33 ± 0.04	B–F(4)	1.23 ± 0.05

structures[26] of NH_4BF_4 and $RbBF_4$ indicate that no great error is introduced by assuming the packing radii of F^- and a fluorine atom in BF_4^- to be equivalent. The B–F distances range from 1.23 to 1.34 A. Values of 1.40–1.43 A have been reported in simple tetrafluoroborate salts,[27] but in other examples,[19] where disorder affects the results of the analysis, values of close to 1.30 A have been found. As the fluorine atoms all have large amplitudes of thermal vibration, we think that the short B–F distances found in the present structure are, in part, a consequence of librational motion of the anion. We do not consider, however, that our present data warrant a quantitative treatment of this motion. In particular, the very short B–F(4) distance cannot be entirely explained in terms of large libration affecting F(4), and we conclude that the positioning of this atom from our analysis is in error because of the poor definition of detail in this region of the cell.

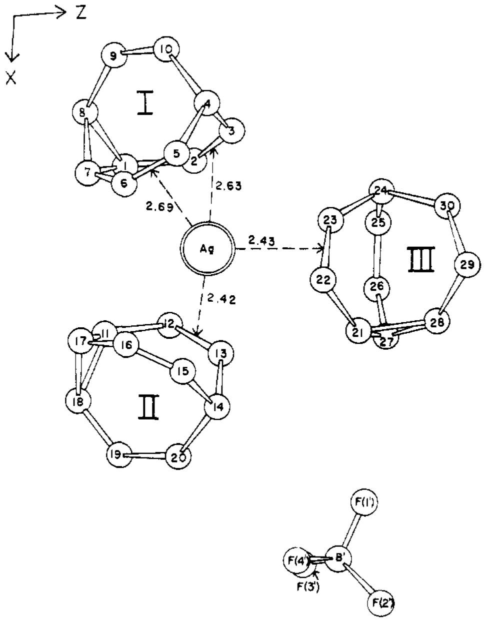

Figure 1. View of the complex looking along the *b* axis. Distances of Ag^+ to the midpoints of double bonds involved in strong complex formation are shown in angstrom units.

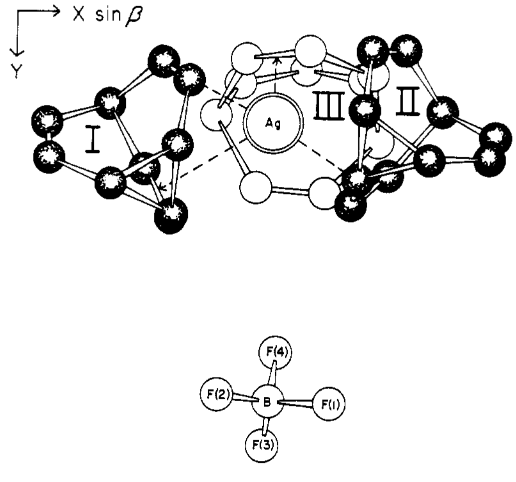

Figure 2. View of the molecule looking along the *c* axis. The carbon atoms of bullvalene molecules I and II are shaded to bring out the spatial relationships of the three molecules.

Diffraction effects from the silver ion could well cause errors in the positions of F(3) and F(4), as these atoms have *x* and *z* coordinates almost identical with those of the silver atom. Such effects were also apparent in the cyclooctatetraene–silver nitrate analysis.[22]

The two largest positive peaks in a difference map, computed at the end of the analysis, were situated quite near F(4′). The actual positions are shown in Figure 4. The heights of these peaks were 0.38 and 0.37 e A^{-3} compared to heights of 1.3–1.8 e A^{-3} for the fluorine atoms in the final electron density map.

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(26) J. L. Hoard and V. Blair, *J. Am. Chem. Soc.*, 57, 1985 (1935).

(27) L. E. Sutton in "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, M 18.

Table IV. Bond Angles (deg) in the Bullvalene Molecules

C(2)	C(1)	C(7)	123 ± 2	C(12)	C(11)	C(17)	131 ± 2	C(22)	C(21)	C(27)	123 ± 3
C(2)	C(1)	C(8)	120 ± 2	C(12)	C(11)	C(18)	124 ± 3	C(22)	C(21)	C(28)	112 ± 2
C(7)	C(1)	C(8)	59 ± 2	C(17)	C(11)	C(18)	63 ± 2	C(27)	C(21)	C(28)	61 ± 3
C(1)	C(2)	C(3)	127 ± 2	C(11)	C(12)	C(13)	123 ± 3	C(21)	C(22)	C(23)	134 ± 3
C(2)	C(3)	C(4)	122 ± 2	C(12)	C(13)	C(14)	124 ± 2	C(22)	C(23)	C(24)	121 ± 2
C(3)	C(4)	C(5)	108 ± 2	C(13)	C(14)	C(15)	109 ± 2	C(23)	C(24)	C(25)	111 ± 2
C(3)	C(4)	C(10)	109 ± 2	C(13)	C(14)	C(20)	105 ± 2	C(23)	C(24)	C(30)	102 ± 2
C(5)	C(4)	C(10)	116 ± 2	C(15)	C(14)	C(20)	108 ± 2	C(25)	C(24)	C(30)	109 ± 2
C(4)	C(5)	C(6)	123 ± 2	C(14)	C(15)	C(16)	126 ± 2	C(24)	C(25)	C(26)	122 ± 3
C(5)	C(6)	C(7)	127 ± 2	C(15)	C(16)	C(17)	128 ± 2	C(25)	C(26)	C(27)	131 ± 2
C(1)	C(7)	C(6)	121 ± 2	C(11)	C(17)	C(16)	120 ± 2	C(21)	C(27)	C(26)	122 ± 3
C(1)	C(7)	C(8)	61 ± 2	C(11)	C(17)	C(18)	64 ± 2	C(21)	C(27)	C(28)	69 ± 2
C(6)	C(7)	C(8)	121 ± 2	C(16)	C(17)	C(18)	117 ± 2	C(26)	C(27)	C(28)	118 ± 2
C(1)	C(8)	C(7)	60 ± 2	C(11)	C(18)	C(17)	53 ± 3	C(21)	C(28)	C(27)	50 ± 2
C(1)	C(8)	C(9)	123 ± 2	C(11)	C(18)	C(19)	120 ± 2	C(21)	C(28)	C(29)	124 ± 3
C(7)	C(8)	C(9)	125 ± 1	C(17)	C(18)	C(19)	127 ± 2	C(27)	C(28)	C(29)	125 ± 2
C(8)	C(9)	C(10)	126 ± 2	C(18)	C(19)	C(20)	127 ± 2	C(28)	C(29)	C(30)	131 ± 3
C(4)	C(10)	C(9)	124 ± 2	C(14)	C(20)	C(19)	129 ± 3	C(24)	C(30)	C(29)	126 ± 2

The Ag^+ ion deviates by 0.10 A from the plane through the centers of mass of the three complexed bullvalene molecules. These three molecules are grouped around the Ag^+ ion in positions close to those related by a threefold rotation axis normal to an approximate plane containing the centers of mass of the three molecules and passing through the Ag^+ ion. The angles subtended to the central ion by the centers of mass of molecules I and II, II and III, and I and III are 113, 130, and 117°, respectively. The Ag^+–C(sp^2) distances are given in Table III, and the distances of the metal ion to the midpoint of the double bonds involved in complex formation are shown in Figure 1.

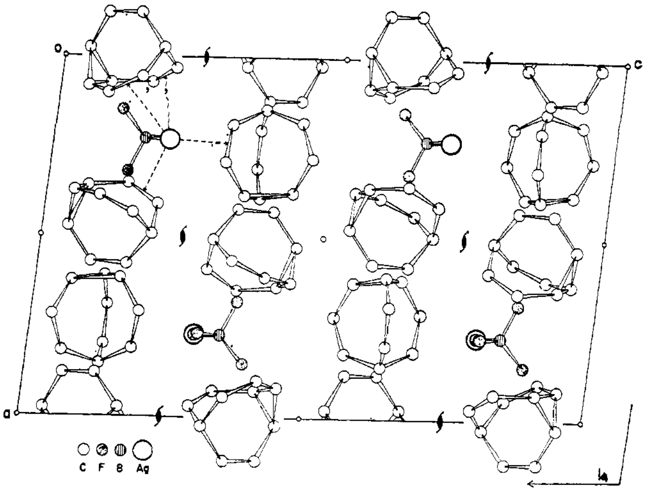

Figure 3. The *ac*-packing diagram showing the contents of a complete unit cell.

In molecule I, the Ag^+ ion is effectively equidistant (2.63 and 2.69 A) from the midpoints of the C(2)–C(3) and C(5)–C(6) double bonds. In both cases, however, the individual Ag^+–C(sp^2) distances are significantly unequal, indicating that the silver ion is positioned asymmetrically with respect to the two carbon atoms forming the double bond. Similar asymmetries have been found in many other Ag^+–olefin complexes studied crystallographically,[22–24] and it is unlikely that the effect can be entirely attributed to packing forces. The asymmetric position of the Ag^+ ion with respect to the two C(sp^2) atoms may be the result of a compromise between the optimum position for maximum overlap of a donor π orbital, symmetrically distributed between the two carbon atoms of the olefin, with a vacant orbital of the Ag^+ ion, and the position allowing maximum overlap of a filled d or dp orbital on the metal with a vacant antibonding π^* orbital of the olefin.[28] The geometry of the complex and the symmetry of the π^* orbital on the olefin would only permit overlap with one of the lobes of this orbital, resulting in a closer approach of the metal ion to the atom bearing the lobe involved in bonding.

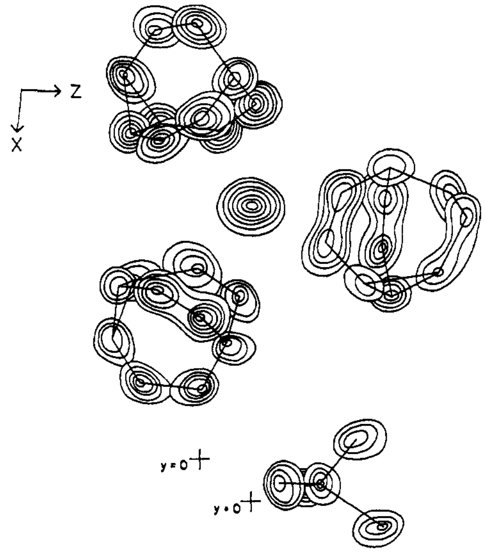

Figure 4. The final electron density distribution, shown as a superimposed contour diagram of that part of the unit cell shown in Figure 1. The contour interval for the Ag^+ ion is ten times greater than that for the other atoms. The positions of the two largest peaks in the difference map are marked by crosses. Certain features of molecule III are not very well resolved.

Unequal metal–C(sp^2) distances are also found in olefin–Cu(I) chloride complexes,[29,30] where the asymmetric effects can also be inferred from the distortion of the trigonal configuration about Cu, and where the

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[28] M. J. S. Dewar, *Bull. Soc. Chim. France*, 18, C79 (1951).

[29] N. C. Baenziger, G. F. Richards, and J. R. Doyle, *Inorg. Chem.*, 3, 1529 (1964).

[30] N. C. Baenziger, H. L. Haight, and J. R. Doyle, *ibid.*, 3, 1535 (1964).

location of two of the bonding orbitals of the Cu atom is known from the direction of the Cu–Cl bonds. Similar ideas have been invoked by Turner and Amma[31] to explain asymmetry in Ag^+–aromatic interactions.

The Ag^+ ion probably interacts with two double bonds in bullvalene molecules II and III. The distances from Ag^+ to the midpoint of the C(12)–C(13) double bond in molecule II and to the midpoint of the C(22)–C(23) double bond in molecule III are indicative of fairly strong interactions. The values of 2.42 and 2.43 A almost equal the shortest contact (2.38 A) in the cyclooctatetraene–silver nitrate complex[22] and approach the Ag^+–midpoint distances calculated for the humulene–silver nitrate adduct (2.29 A in each case)[23] and for the norbornadiene–silver nitrate complex (2.26 A),[24] where the metal is associated with only one olefinic bond. The Ag^+–C(sp^2) distances for the C(12)–C(13) and C(22)–C(23) contacts also display the asymmetry noted above. In molecules II and III, there is also a much longer contact involving the C(15)–C(16) and C(25)–C(26) double bonds. It is questionable whether these contacts imply substantial interaction (see discussion in ref 29), although distances of similar length were observed in the cyclooctatetraene–silver nitrate crystal.[22]

The interaction of Ag^+ with molecule I is the first reported example where the metal is equidistant to two olefinic bonds, apart from the rather poorly defined structure of the silver nitrate adduct of the cyclooctatetraene dimer,[32] where the interaction is with bonds in two separate molecules. The angle between the plane (Ag, C(2), C(3)) and the best plane (C(1), C(2), C(3), C(4)) is 91.5°, and the angle between the plane (Ag, C(5), C(6)) and the best plane (C(4), C(5), C(6), C(7)) is 91.1°. Maximum overlap of an orbital on the metal with the π orbital of the olefin would be expected to occur when these planes are normal to each other. Deviations of the corresponding angles from 90° have been noted in the case of the cyclooctatetraene–$AgNO_3$ complex (104.7° for the shortest contact and 93.2° for the longer contact),[22] the norbornadiene–$2AgNO_3$ complex (113.2°),[24] the cyclooctatetraene–CuCl complex (109.2°),[29] and the norbornadiene–CuCl complex (109.1°).[30] The corresponding angles are 103 and 104.4° for the interaction of Ag^+ with C(12)–C(13) in molecule II and with C(22)–C(23) in molecule III. In the humulene–$2AgNO_3$ adduct,[23] which is the only reported case of Ag^+ complexing to a *trans* double bond, the angles are much closer to 90° (85 and 87°), but there are large distortions from planarity of the olefin groups. We can offer no explanation why there should be an approximately equal interaction with two double bonds in molecule I, with the Ag^+ atom in a position allowing almost maximum overlap with the π orbitals of the double bonds, while there is a *stronger* interaction (as inferred from the distances) with only *one* double bond in molecules II and III, where the Ag^+ atom occupies a position significantly different from that corresponding to maximum overlap.

The deviation of the silver atom from the plane defined by the midpoint of the C(12)–C(13) bond, the midpoint of the C(22)–C(23) bond, and the center of mass of molecule I is 0.08 A. In cyclooctatetraene–$AgNO_3$,[22] the Ag^+ ion deviated by 0.07 A from the plane defined by the two nearest oxygen atoms in the nitrate groups and the midpoint of the double bond involved in the shortest contact. In norbornadiene–$2AgNO_3$,[24] the deviation of Ag^+ from a similarly defined plane was 0.09 A. The distance between the midpoints of the two complexing double bonds in molecule I is 2.76 A, as compared to a distance of 3.10 A between the midpoints of the C(1)–C(2) and C(5)–C(6) double bonds in the cyclooctatetraene molecule involved in complex formation.[22]

The bond distances and angles in molecule I are very close to predicted values. This is not true, however, of molecules II and III. Inspection of Tables III and IV shows that in these molecules there are differences of four or five times the estimated standard deviations from expected dimensions, especially involving the unique bridgehead methine carbon atoms, C(14) and C(24), and the carbon atoms of the three-membered ring. The standard deviations for the atoms of these molecules are certainly underestimated, as they do not take account of the disorder, described below. C(sp^3)–C(sp^2) distances involving the unique bridgehead methine range from 1.47 to 1.74 A, and the C–C distances in the three-membered ring range from 1.43 to 1.77 A. In comparing molecules II and III, a definite pattern is observed for dimensions which bear the same spatial relationship to the double bonds involved in short and long Ag^+ contacts. For example, the C(11)–C(17) and C(21)–C(27) bonds in the three-membered ring are both short, 1.43 and 1.45 A, while the C(11)–C(18) and C(21)–C(28) bonds are both long, 1.60 and 1.77 A; the bonds C(13)–C(14) and C(23)–C(24) adjacent to the strongly complexed double bond are longer, 1.66 and 1.74 A, than the other bonds involving the unique bridgehead methine carbon atom (1.47–1.61 A); the angle in the three-membered ring subtended by the two carbon atoms adjacent to the complexing double bonds is very much less than 60°, while the other two angles in the three-membered ring are greater than 60°. The temperature factors for the atoms in molecules II and III are somewhat greater than those in molecule I. The striking contrast between the dimensions obtained for molecule I and those found in molecules II and III, and the correspondence in the values found in the latter two cases, lead us to conclude that the effect is probably due to minor disorder involving molecules II and III. The position of the double bond involved in the stronger complex formation is fixed and occupies the same position in all unit cells, but in a small number of unit cells there is a reorientation of the molecule with the three-membered ring taking over the position occupied by the unique bridgehead methine atom in the predominant number of unit cells and *vice versa*. Such an effect could account for the poor definition of atomic positions in these two molecules and the unusual molecular dimensions that are measured. The disorder may be caused by valence tautomerism taking place in the crystal. A strong silver complex with two of the three double bonds in bullvalene is sufficient to "freeze" the tautomer, as a self-rearrangement pathway requires the mobility of two double bonds. Assuming that the longer Ag^+–olefin contact does not represent a sufficiently strong interaction to "freeze" that double bond,

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(31) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 1877 (1966).

(32) S. C. Nyburg and J. Hilton, *Acta Cryst.*, **12**, 116 (1959).

there is one rearrangement pathway available to molecules II and III, but none in molecule I. While we certainly do not intend to imply that the molecular arrangement found in the crystal is identical with that occurring in solution,[33] one can nevertheless conceive of several models which would be consistent with the reduced rate of self-rearrangement measured by Allerhand and Gutowsky.[8] We, therefore, feel compelled to add a qualification to our initial conclusion[2] that there was no evidence for valence tautomerism in the crystal.

The infrared spectrum of the 2:1 complex has bands at 1620 and 1565 cm^{-1}, typical[34] of complexed and uncomplexed olefinic double bonds, and that of the 3:1 complex shows bands at 1625 and 1575 cm^{-1}.

Conclusions

1. The crystalline $(bullvalene)_3AgBF_4$ complex has been shown to consist of discrete $(bullvalene)_3Ag^+$ units without involvement of the tetrafluoroborate anions in covalent bonding.
2. The Ag^+ ion complexes to two double bonds in one of the bullvalene molecules but interacts strongly with only one double bond in the other two molecules.
3. All the short $Ag^+\cdots C{=}C$ contacts show the metal ion placed asymmetrically with respect to the two carbon atoms, a phenomenon which might be explained in terms of back-donation of electrons from the metal to a π^* orbital of the olefin.
4. The Ag^+ atom, when interacting with a single double bond in a molecule, deviates by a substantial angle from a position normal to the plane of the olefinic group.
5. There is evidence for disorder involving those portions of molecules II and III not involved in complex formation. This may be caused by valence tautomerism occurring in the crystal.[34a]

Acknowledgment. We wish to thank Professor H. S. Gutowsky, who suggested the problem, and Dr. A. Allerhand, who provided us with samples of the bullvalene–silver salt complexes which he had prepared. The bullvalene used in the present study came from Dr. Gerhard Schröder through the courtesy of Union Carbide Research Institute. Later samples were obtained from Dr. Schröder directly. The detailed computations were carried out on the IBM 7094 at the University of Illinois, and the expenses involved therein were partially defrayed by a grant from the University of Illinois Graduate College Research Board.

Table V. Intermolecular Contacts (A) Less Than 3.70 A[a]

C(7)···C(11)	3.49	C(19)···C(21)[b]	3.68
C(1)···C(12)	3.53	C(19)···C(28)[b]	3.68
C(2)···C(12)	3.56	F(1)···C(27)[b]	3.57
C(6)···C(16)	3.56	F(4)···C(20)[b]	3.48
C(6)···C(17)	3.59	C(5)···F(3)[c]	3.36
C(7)···C(17)	3.66	C(15)···F(1)[c]	3.66
C(13)···C(22)	3.61	C(15)···F(3)[c]	3.68
C(14)...C(22)	3.69	C(16)···F(1)[c]	3.59
C(15)···C(22)	3.61	C(22)···F(3)[c]	3.22
C(3)···C(23)	3.54	C(23)···F(3)[c]	3.39
C(5)···C(23)	3.61	C(29)···F(1)[d]	3.59
C(3)···C(24)	3.61	C(29)···F(2)[d]	3.66
C(13)···C(26)	3.60	F(2)···C(24)[e]	3.65
C(13)···C(27)	3.60	C(6)···C(8)[f]	3.59
C(1)···F(2)	3.53	C(6)···C(9)[f]	3.66
C(2)···F(2)	3.61	C(8)···F(2)[g]	3.67
C(2)···F(4)	3.34		
C(12)···F(4)	3.47		

[a] Superscripts denote transformations of the coordinates listed in Table I. [b] Denotes atoms related by $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$. [c] Denotes atoms related by $x, -1 + y, z$. [d] Denotes atoms related by $x, \frac{1}{2} - y, \frac{1}{2} + z$. [e] Denotes atoms related by $-x, \frac{1}{2} + y, \frac{1}{2} - z$. [f] Denotes atoms related by $-x, -y, -z$. [g] Denotes atoms related by $-x, 1 - y, -z$.

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(33) In the case of Ag^+ complexes of norbornadiene, a 1:1 complex, possessing a C=C stretching vibration, typical of uncomplexed olefins, has been demonstrated in solution,[15] whereas the crystal structure shows a $C_7H_8 \cdot 2AgNO_3$ complex with both double bonds complexed.[24]

(34) H. W. Quinn, J. S. McIntyre, and D. J. Peterson, *Can. J. Chem.*, **43**, 2896 (1965).

(34a) NOTE ADDED IN PROOF. As we go to press, the crystal structure of a (1:1) bullvalene–$AgBF_4$ complex, which has two crystallographically independent $(C_{10}H_{10})AgBF_4$ groups in the asymmetric unit, has been solved in this laboratory. The olefin and Ag^+ ions alternate in an infinite spiral or helix around a crystallographic 2_1 screw axis. Full details will be published in the near future.