$$c_{\text{tot}} = c_1 + 2c_2 = c_{10} = 2c_{2\infty}$$

$$D_+ = \epsilon_1 c_1 + \epsilon_2 c_2 \qquad D_0 = \epsilon_1 c_{10} \qquad D_\infty = \epsilon_2 c_{2\infty}$$

$$D_0 - D_+ = \epsilon_1 c_1 + 2\epsilon_1 c_2 - \epsilon_1 c_1 - \epsilon_2 c_2 = c_2(2\epsilon_1 - \epsilon_2)$$

$$D_+ - D_\infty = \epsilon_1 c_1 + \epsilon_2 c_2 - \epsilon_2 c_{2\infty} = [(\epsilon_1 c_1 - \epsilon_2 c_2 - \epsilon_2 c_1)/2] - \epsilon_2 c_2 = c_1(\epsilon_1 - \epsilon_2/2)$$

$$\frac{D_0 - D_+}{(D_+ - D_\infty)^2} = \frac{2c_2[\epsilon_1 - \epsilon_2/2]}{c_1{}^2[\epsilon_1 - \epsilon_2/2]^2} = \frac{c_2}{c_1{}^2[\epsilon_1 - \epsilon_2/2]} \qquad (2)$$

Therefore,

$$\log\left[\frac{(D_0 - D_+)}{(D_+ - D_\infty)^2}\right] = \log K_D - 2\log[H^+] + \log A$$

and

$$A = 2/[\epsilon_1 - \epsilon_2/2]$$

If we define $pH = -\log[H^+]$, then a plot of $\log[(D_0 - D_+)/(D_+ - D_\infty)^2]$ *vs.* pH should be a straight line with slope 2 and intercept $\log K_D + \log A$. Since $\log A$ can be experimentally measured, the equilibrium constant K_D can be determined.

Metal Ion–Aromatic Complexes. XI. The Crystal and Molecular Structure of Bis(cyclohexylbenzene)silver(I) Perchlorate

E. A. Hall Griffith[1] **and E. L. Amma***

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received September 9, 1970*

Abstract: The crystal and molecular structure of bis(cyclohexylbenzene)silver(I) perchlorate, $(C_6H_{11}C_6H_5)_2AgClO_4$, has been determined by single-crystal X-ray diffraction from 981 counter intensities measured at ambient room temperature. The crystals were found to be orthorhombic: $a = 32.17$ (2), $b = 5.666$ (3), $c = 12.67$ (1) Å; $Z = 4$; space group *Pmcn*. The structure was refined by full-matrix least squares to a final conventional R factor of 0.069. The crystal structure is composed of alternating layers of $AgClO_4$ and hydrocarbon which are of infinite extent in the *bc* plane. The molecular structure is described in terms of a "half-open hinge" with the connecting section removed and a silver ion displaced toward the open end of the hinge. The leaves of the "hinge" are the organic groups. The Ag(I) is three-coordinate with one donor bond from each of the two aromatic rings and the third interaction with an oxygen of the perchlorate group. The angular relationships between the three donors are such that it appears the silver is using either 5p or $5s5p^3$ orbitals as acceptors. The $AgClO_4$ chains propagate parallel to the *b* axis and are held together by weak Ag–O interactions and van der Waals forces. The silver–aromatic interaction is asymmetric, having Ag–C distances of 2.48 (1) and 2.66 (1) Å and Ag–C–C angles of 66 (1) and 82 (1)°.

Complexes formed between aromatic moieties and silver(I) were first described by Hill during the course of phase studies early in the 1920's,[2-4] but nearly 30 years elapsed before more significant work on these donor-acceptor complexes was reported. Both Mulliken[5] and Dewar[6] formulated theoretical models for the bonding in silver perchlorate–benzene, and the gross features of their models were verified by the crystal structures of $C_6H_6 \cdot AgClO_4$[7,8] and of $C_6H_6 \cdot AgAlCl_4$.[9] However, these structure results complicate the theoretical model that assumes a 1:1 interaction between the aromatic moiety and the silver ion. In the former case each silver ion is π bonded to two benzene rings such that a polymer, –Ar–Ag–Ar–Ag–, is formed, whereas in the latter case the silver ion is π bonded to only one benzene ring but interacts with four chlorine atoms to yield a five-coordinate Ag^+. There was extensive evidence from solution equilibrium studies of silver salts in aromatic–water systems, as reviewed by Andrews,[10] for the existence of complexes of the types $AgAr^+$ and Ag_2Ar^{2+}. Other solution work[11-16] indicated that stoichiometries other than one silver per aromatic were possible, but the first well-characterized crystalline complex of the type $AgAr_2^+$ was that of bis(cyclohexylbenzene)silver perchlorate, for which a preliminary communication has been published[17] and for which we wish to report here the synthetic and structural details.

The structures of two other complexes of the $AgAr_2^+$ type, bis(*m*-xylene)silver perchlorate[18] and bis(*o*-xylene)silver perchlorate[19] have now been published. More

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novel stoichiometries were revealed in the structure studies of naphthalenetetrakis(silver perchlorate) tetrahydrate and anthracenetetrakis(silver perchlorate) monohydrate.[20] These complexes comprise part of a systematic examination of the Ag(I)–aromatic interaction so that the relative roles of steric, electronic, molecular packing, and other effects might be ascertained. Other such complexes now under investigation include (p-xylene)$_2\cdot$AgClO$_4$, indene$\cdot$AgClO$_4$, (s-mesitylene)$_2\cdot$AgClO$_4$, bibenzyl$\cdot$AgClO$_4$,[21] acenaphthene$\cdot$AgClO$_4$,[22] acenaphthalene$\cdot$AgClO$_4$,[22] 1-methylnaphthalene$\cdot$4AgClO$_4$,[22] and (s-mesitylene)$_2\cdot$AgCOOCF$_3$.

Experimental Section

Anhydrous silver perchlorate (2.0 g) was dissolved in 15 ml of cyclohexylbenzene with gentle warming and the resulting solution allowed to cool slowly in an anhydrous environment. After several days, flattened needles of the colorless complex, bis(cyclohexylbenzene)silver(I) perchlorate, formed in a dark reddish brown oil. Potentiometric titrations of ~0.1-g samples yielded consistently low silver analyses owing to a persistent coating of oil on the crystals (*Anal.* Calcd for (C$_6$H$_{11}$C$_6$H$_5$)$_2$AgClO$_4$: Ag, 20.48. Found: Ag, 18.73). Inasmuch as the crystals are hygroscopic, light sensitive, and stable only under a positive vapor pressure of cyclohexylbenzene, they were sealed in thin-walled glass capillaries for diffraction studies.

Preliminary Weissenberg and precession photographic data, $hk0$, $hk1$, . . . , $hk9$, $h0l$, $0kl$, were used to establish the probable space groups. The observed systematic absences (for $h0l$, $l = 2n + 1$ and for $hk0$, $h + k = 2n + 1$) specified the possible orthorhombic space groups as $Pmcn$ or $P2_1cn$.[23] The structure analysis established the space group as $Pmcn$, *vide infra.* A least-squares fit of the χ, ϕ, and 2θ angles of 30 reflections accurately centered on a Picker full-circle automatic diffractometer were used to determine the lattice constants at ambient room temperature (λ 0.71068): $a = 32.17$ (2), $b = 5.666$ (3), $c = 12.67$ (1) Å. Because of the high solubility in bromoform–carbon tetrachloride solutions, the density could only be approximated as *ca.* 1.4 g cm^{-3}. This compares favorably to a calculated density, with four molecules per cell, of 1.52 g cm^{-3}.

A crystal 0.34 × 0.16 × 1.3 mm, which was aligned with the needle direction "c" parallel to the capillary length and the axis of the goniometer head, was used to collect the X-ray diffraction intensity data. The linear absorption factor (μ) for this compound with Mo Kα radiation is only 11 cm^{-1}. No corrections were made for absorption because absorption due to the oil coating the crystal and the glass of the capillary probably outweighs simple absorption effects.

A manual recording of 1650 independent reflections was made at ambient room temperature with Zr-filtered Mo Kα radiation on a Picker diffractometer with a General Electric single-crystal orienter. Each reflection was measured by a θ–2θ scan for 100 sec at the rate of 0.0168°/sec, while the backgrounds were estimated by stationary counting for 40 sec at ±0.84° of 2θ from peak maximum. Integrated intensities were calculated, assuming a linear variation in background, from the function $I_{\text{net}} = I_{\text{scan}} - 1.25(B_1 + B_2)$ where B_1 and B_2 are the background counts. Reflections were considered to be absent if the integrated net intensity was less than $2.68[1.25(B_1 + B_2)]^{1/2}$ (2.68σ of background). Of the 1650 measured reflections 981 were considered nonzero by this criteria.

A standard reflection was measured every two hours to ensure stability of electronic operation, to monitor crystal decomposition, and to provide a basis for the scaling of the data. An analysis of the standard peak revealed that the crystal underwent a gradual decomposition, but that variation from one standard peak to the next was less than 0.5% of the total count. During the data collection period of 1 month there was an overall loss of intensity of some 22%. In order to compensate for this loss I_{net} was scaled by I_t/I_0, where I_0 is the integrated intensity of the median standard peak and I_t is the integrated intensity of the standard peak taken immediately prior to the general peak.

The takeoff angle, source-to-crystal, and crystal-to-counter values were 3.7°, 18 cm, and 23 cm, respectively, and the receiving aperture at the counter was 6 mm wide × 8 mm high. The half-width at half-peak height for an average reflection was 0.7° in 2θ at the 3.7° takeoff angle, indicating a mosaic spread such that all the reflection was counted during the scan. This 0.7° should not be interpreted as an absolute value of the mosaic spread, since this quantity depends upon instrumental factors as well. Attenuation filters were used so that the counting rate never exceeded 5000 counts/sec. The usual Lorentz–polarization corrections were made and intensities were reduced to structure factors. Corrections for anomalous dispersion effects were included in the refinement.

Solution of Structure

With four bis(cyclohexylbenzene)silver perchlorate units per cell, the silver and perchlorate ions are required to lie on one of the three fourfold sets of special positions and the cyclohexylbenzene moiety must be located in the general positions of space group $Pmcn$, $\pm(x, y, z;\ {}^1/_2 + x, \bar{y}, \bar{z};\ {}^1/_2 + x, {}^1/_2 + y, {}^1/_2 - z;\ x, {}^1/_2 - y, {}^1/_2 + z)$. Inasmuch as it is impossible to place a tetrahedral perchlorate group on a crystallographic center of symmetry, the chlorine and two oxygens atoms are constrained to lie in the mirror at $x = {}^1/_4$. The silver ions may lie in the mirror as well or on one of the two possible sets of centers. Examination of an unsharpened three-dimensional Patterson vector map[24] revealed that the silver was indeed located on the mirror, and coordinates for the silver and chlorine atoms were readily sorted out from the possible ambiguities inherent in an orthorhombic vector map. A structure factor calculation based on these coordinates yielded a disagreement index R of 0.33, and the phases from this calculation were used to compute a three-dimensional electron density map from which all of the nonhydrogen atoms were located. Several cycles of full-matrix least-squares refinement reduced the R factor to 0.15, and a three-dimensional difference Fourier map indicated appreciable anisotropic thermal motions for the atoms. The full-matrix fully anisotropic refinement[25] converged to values of 0.069, 0.069, and 2.66 for R, the weighted R, and the standard error of an observation of unit weight.[26] On the final cycle of refinement the parameter shifts were all less than one-tenth of a standard deviation. A final difference electron density map was qualitatively featureless.

The function minimized was $\Sigma w(F_o - F_c)^2$ with unit weights. Scattering factors for Ag$^+$, Cl$^-$, and neutral oxygen and carbon were from Cromer and Waber.[27] The effects on anomalous dispersion were included in the structure factor calculations by addition to F_c;[28] the values for $\Delta f'$ and $\Delta f''$ for silver and chlorine were those given by Cromer.[29] The final tabulation of observed and calculated structure factors are filed elsewhere.[30]

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Table I. Final Atomic Positional and Thermal Parameters and Estimated Standard Deviations[a,b]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*x*
Ag	0.2500 (−)	0.1951 (3)	0.0910 (2)	C(5)	0.3388 (4)	0.3894 (18)	0.0710 (10)
Cl	0.2500 (−)	0.7616 (7)	0.9250 (4)	C(6)	0.3128 (3)	0.3987 (21)	0.1578 (10)
O(1)	0.2500 (−)	0.5062 (21)	0.9340 (13)	C(7)	0.3946 (3)	0.3057 (23)	0.4613 (10)
O(2)	0.2500 (−)	0.8361 (47)	0.8155 (14)	C(8)	0.4387 (3)	0.2413 (31)	0.4961 (11)
O(3)	0.2862 (4)	0.8510 (22)	0.9566 (17)	C(9)	0.4687 (4)	0.2215 (31)	0.4032 (13)
C(1)	0.3119 (3)	0.2122 (24)	0.2320 (10)	C(10)	0.4682 (5)	0.4458 (33)	0.3383 (13)
C(2)	0.3381 (4)	0.0097 (22)	0.2145 (10)	C(11)	0.4236 (5)	0.5130 (28)	0.3020 (12)
C(3)	0.3645 (3)	0.0083 (21)	0.1325 (11)	C(12)	0.3950 (4)	0.5335 (24)	0.3986 (12)
C(4)	0.3655 (3)	0.1919 (20)	0.0537 (10)				

Atom	β_{11}	β_{22}	β_{33}	β_{13}	β_{12}	β_{23}
Ag	10 (1)	547 (7)	136 (2)	0 (−)	0 (−)	−120 (4)
Cl	10 (1)	288 (15)	69 (5)	0 (−)	0 (−)	14 (7)
O(1)	21 (2)	262 (43)	140 17)	0 (−)	0 (−)	58 (22)
O(2)	46 (5)	1612 (172)	64 (18)	0 (−)	0 (−)	241 (48)
O(3)	26 (2)	571 (56)	496 (36)	−21 (9)	−74 (7)	43 (37)
C(1)	11 (1)	448 (51)	37 (12)	−19 (7)	1 (3)	8 (21)
C(2)	11 (1)	374 (48)	55 (14)	−10 (7)	−1 (3)	−35 (19)
C(3)	1 (1)	318 (47)	56 (13)	−7 (6)	−2 (3)	1 (18)
C(4)	8 (1)	307 (43)	55 (12)	−10 (6)	−5 (3)	−16 (19)
C(5)	11 (1)	265 (36)	54 (13)	−4 (5)	2 (3)	−49 (17)
C(6)	8 (1)	433 (56)	31 (12)	−2 (6)	−2 (3)	−60 (19)
C(7)	11 (1)	400 (52)	55 (12)	3 (7)	3 (3)	5 (20)
C(8)	10 (1)	762 (77)	57 (12)	21 (9)	8 (3)	77 (26)
C(9)	17 (2)	720 (79)	90 (16)	22 (10)	14 (5)	58 (35)
C(10)	18 (2)	782 (94)	85 (18)	10 (12)	19 (5)	98 (33)
C(11)	15 (2)	659 (7)	64 (15)	−2 (10)	1 (5)	60 (26)
C(12)	14 (2)	497 (55)	58 (14)	15 (7)	8 (4)	63 (25)

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. (−) indicates a fixed parameter. [b] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$.

Unobserved data were not used in the structure refinement, but are listed with the calculated structure factors elsewhere.[30] Final atomic positional and thermal parameters are in Table I. Interatomic distances and angles and dihedral angles between normals to planes and their errors[31a] were computed using the last cycle of least squares and are listed in Table II. Root-mean-square components of thermal displacement[31a] are listed in Table III. The least-squares plane[31b] for the aromatic group is listed in Table IV.

Description and Discussion

The gross crystal structure is composed of alternating layers of "ionic matter" ($AgClO_4$) and "insulation" (hydrocarbon) which are of infinite extent in the *bc* plane (Figures 1 and 2). The molecular environment of the silver(I) species may be described in terms of a "half-open hinge" with the connecting section removed and the silver ion displaced toward the open end of the hinge and located in the crystallographic mirror which is the bisector of the hinge. The two organic groups which are related by the mirror act as the leaves of the hinge (Figure 1) and are oriented at an angle of 89 (1)° relative to each other.

Table II. Interatomic Distances and Angles[a]

	Bond Lengths, Å		
Ag–C(1)	2.68 (1)	C(1)–C(2)	1.44 (2)
Ag–C(6)	2.48 (1)	C(1)–C(6)	1.42 (2)
Ag–O(1*)	2.66 (1)	C(2)–C(3)	1.34 (2)
Ag–O(3)	2.84 (2)	C(3)–C(4)	1.44 (2)
Ag–O(3′)	2.84 (2)	C(4)–C(5)	1.43 (2)
		C(4)–C(7)	1.50 (2)
Cl–O(1)	1.45 (1)	C(5)–C(6)	1.38 (2)
Cl–O(2)	1.45 (2)	C(7)–C(8)	1.53 (2)
Cl–O(3)	1.33 (1)	C(7)–C(12)	1.52 (2)
Cl–O(3′)	1.33 (1)	C(8)–C(9)	1.53 (2)
		C(9)–C(10)	1.51 (2)
O(1)–O(2)	2.40 (2)	C(10)–C(11)	1.55 (2)
O(1)–O(3)	2.29 (2)	C(11)–C(12)	1.54 (2)
O(2)–O(3)	2.14 (2)		
O(1*)–O(3)	3.90 (2)		
	Angles, Deg		
C(1)–Ag–C(6)	32 (1)	C(2)–C(1)–C(6)	119 (1)
C(1)–Ag–C(1′)	96 (1)	C(1)–C(2)–C(3)	120 (1)
C(6)–Ag–C(6′)	109 (1)	C(2)–C(3)–C(4)	123 (1)
C(1)–Ag–C(6′)	111 (1)	C(3)–C(4)–C(5)	116 (1)
C(1)–Ag–O(1*)	118 (1)	C(4)–C(5)–C(6)	121 (1)
C(6)–Ag–O(1*)	87 (1)	C(5)–C(6)–C(1)	121 (1)
C(1)–Ag–O(3)	97 (1)	C(3)–C(4)–C(7)	125 (1)
C(6)–Ag–O(3)	101 (1)	C(5)–C(4)–C(7)	119 (1)
Ag–C(1)–C(6)	66 (1)	C(12)–C(7)–C(8)	110 (1)
Ag–C(6)–C(1)	82 (1)	C(7)–C(8)–C(9)	113 (1)
C(6)–O(1*)–C(6′)	70 (1)	C(8)–C(9)–C(10)	111 (1)
O(1*)–C(6)–C(6′)	55 (1)	C(9)–C(10)–C(11)	112 (1)
O(1)–Cl–O(2)	111 (1)	C(10)–C(11)–C(12)	110 (1)
O(1)–Cl–O(3)	111 (1)	C(7)–C(12)–C(11)	111 (1)
O(2)–Cl–O(3)	100 (1)	C(4)–C(7)–C(8)	111 (1)
O(3)–Cl–O(3′)	122 (2)	C(4)–C(7)–C(12)	114 (1)
	Dihedral Angles, Deg		
Benzene ring plane		C(4)–C(7)–C(12)	50 (1)
Benzene ring plane		Benzene ring′ plane	89 (1)

[a] Asterisks refer to atoms in the next cell; primes refer to atoms or molecules related by mirror planes.

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Table III. Rms Component (Å) of Thermal Displacement along Principal Axes[a]

Atom	1	2	3	Atom	1	2	3
Ag	0.23 (1)	0.23 (1)	0.38 (1)	C(5)	0.16 (2)	0.23 (2)	0.26 (2)
Cl	0.21 (1)	0.23 (1)	0.24 (1)	C(6)	0.13 (3)	0.21 (1)	0.28 (2)
O(1)	0.19 (2)	0.34 (2)	0.35 (2)	C(7)	0.21 (2)	0.24 (2)	0.26 (2)
O(2)	0.14 (5)	0.49 (3)	0.54 (3)	C(8)	0.18 (2)	0.23 (2)	0.37 (2)
O(3)	0.25 (2)	0.31 (2)	0.69 (2)	C(9)	0.23 (2)	0.29 (2)	0.38 (2)
C(1)	0.17 (3)	0.22 (2)	0.29 (2)	C(10)	0.19 (3)	0.32 (2)	0.40 (2)
C(2)	0.19 (2)	0.24 (2)	0.27 (2)	C(11)	0.21 (3)	0.29 (2)	0.34 (2)
C(3)	0.21 (2)	0.22 (2)	0.24 (2)	C(12)	0.18 (3)	0.25 (2)	0.33 (2)
C(4)	0.17 (2)	0.23 (2)	0.24 (2)				

[a] Esd's in parentheses.

Table IV. Least-Squares Plane.[a,b] $Ax + By + Cz - D = 0$

Atom	Deviation from plane, Å
C(1)	0.016 (8)
C(2)	−0.021 (9)
C(3)	0.020 (9)
C(4)	−0.026 (8)
C(5)	−0.011 (8)
C(6)	0.010 (8)
C(7)	0.020 (8)

[a] $A = 0.7116$, $B = 0.4518$, $C = 0.5381$, $D = -9.2469$. [b] x, y, z refers to an internal coordinate system. See J. S. Rollett. "Computing Methods in Crystallography," Pergamon Press, Elmsford, N. Y., 1965, p 22. The esd's for the positional parameters of individual atoms were used as weights.

The AgClO$_4$ layers, which are separated by two sheets of hydrocarbon, are made up of –Ag–O$_2$ClOO–Ag– chains propagating parallel to the *b* axis and held together by weak Ag–O interactions and van der Waals forces (Figure 3). Each silver ion is weakly "bonded" at 2.66 (1) Å to an oxygen of a perchlorate group. The next shortest Ag–O distance is 2.84 (2) Å, with two oxygen atoms of a second perchlorate group. It seems unlikely that these individual Ag–O interactions have an appreciable effect in stabilizing the complex since the Ag–O single bond radius sum is 2.18 Å,[32] but the cumulative effect of the Ag–O interactions should not be discounted. Similar weak Ag–O interactions are observed in the structures of benzene–silver perchlorate,[8] naphthalenetetrakis(silver perchlorate) tetrahydrate,[20] and bis(*o*-xylene)silver perchlorate,[19] but much stronger interactions (~2.48 Å) are reported for bis(*m*-xylene)silver perchlorate[18] and anthracenetetrakis(silver perchlorate) monohydrate.[20] Exactly where a significant individual Ag–O interaction begins and ends is a matter of debate, and there probably is not a sharp dividing distance.

The perchlorate ion exhibits a substantial distortion from the idealized tetrahedron. The expected Cl–O distance in the perchlorate ion is 1.43 (2) Å,[33] and the two oxygen atoms which lie in the mirror along with the chlorine atoms exhibit "normal" Cl–O distances of 1.45 (2) Å with the expected associated angles (Table II). On the other hand, the two oxygens which are symmetry related through the mirror have Cl–O distances of 1.33 (1) Å, and the concomitant O(3)–Cl–O(3′) angle has opened up to 122 (2)°. There is no apparent reason for the shortening of these bond distances, but the fact that the 0.12-Å shortening constitutes ~12 standard deviations means that the distortion must be considered to be real. Examination of the final difference Fourier reveals a diffuse scatter of residual electron density around the oxygen positions and would seem to indicate the possibility of a small amount of disorder in the perchlorate ion position. Disorder in structures containing perchlorate ions is well known.[34–37] A second explanation might involve a high thermal motion for the oxygen atoms. Examination of the thermal parameters and the root-mean-square components of the thermal parameters for the atoms of the perchlorate group (Tables I and III) would seem to indicate that the O(3) and O(3′) have no more thermal motion than the other two oxygens and, in fact, have considerably less than O(2), which has no interaction with the silver ion. A third possibility is that nonbonded Ag–O repulsive forces are strong enough to bring about a change in the hybridization of the chlorine by opening up the O–Cl–O angle, which may indirectly shorten these bonds at the expense of the symmetry of the tetrahedron. None of these explanations is completely satisfactory.

The silver coordination may be described as either three- or five-coordinate, depending upon whether the 2.84 (2)-Å Ag–O distances are considered to be long covalent interactions. The three-coordinate description in which each silver is bound to C(6) at 2.48 (1) Å of two aromatic rings and to O(1) at 2.66 (1) Å would seem to be preferable. The C–Ag–C angle of 109 (1)° and the C–Ag–O angles of 87 (1)° tend to indicate that the silver is using either 5p or 5s5p^3 orbitals as acceptors rather than the 5s orbital as proposed by Mulliken[5] and Dewar.[6] Despite this deviation from the theoretical models for the binding in silver(I)–benzene complexes, the results of this structure analysis are in approximate agreement with the prediction that the silver should be oriented above and between the two nearest C–C bonds of the aromatic.

It is significant that all the known silver(I)–aromatic complexes, with the exception of naphthalenetetrakis(silver perchlorate) tetrahydrate,[20] have as a common feature an asymmetric Ag–C interaction with the aromatic, in which the shorter Ag–C distance of 2.47 (2) Å is invariant regardless of stereochemistry, nature of

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(32) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 246.

(33) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions, Supplement 1956–1959," The Chemical Society, London, 1965, p S8s.

(34) R. J. Prosen and K. N. Trueblood, *Acta Crystallogr.*, 9, 741 (1956).

(35) J. D. Lee, D. S. Brown, and B. G. A. Melsom, *ibid., Sect. B*, 25, 1378 (1969).

(36) F. Madaule-Aubry and G. M. Brown, *ibid., Sect. B*, 24, 745 (1968).

(37) F. Madaule-Aubry, W. R. Busing, and G. M. Brown, *ibid., Sect. B*, 24, 754 (1968).

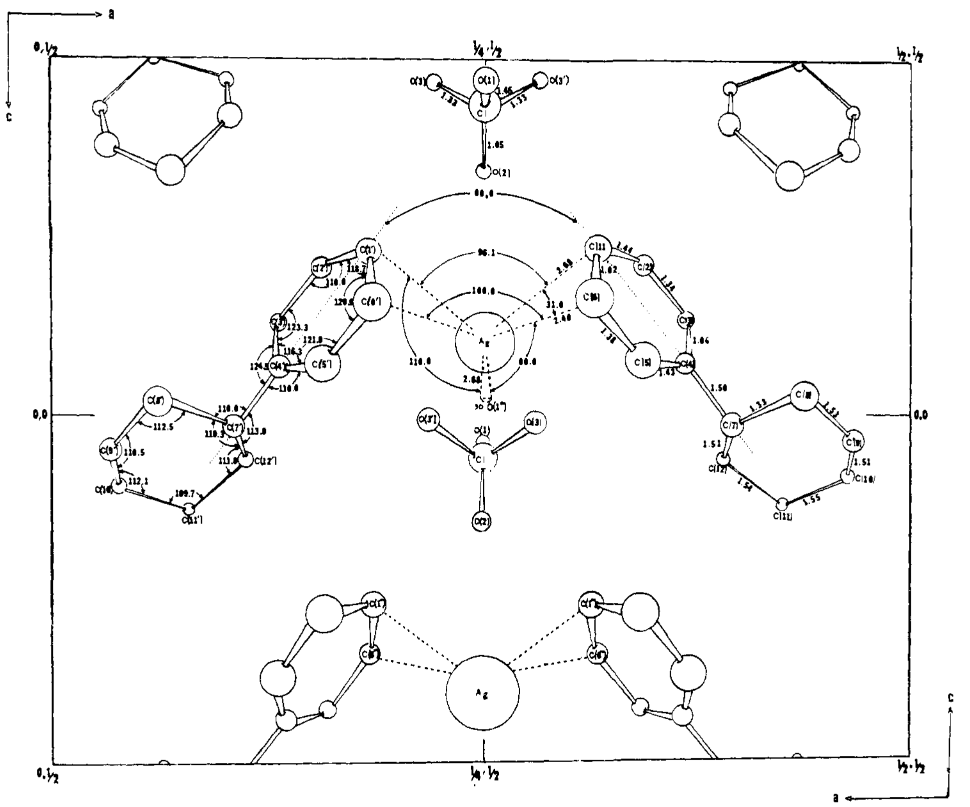

Figure 1. View of a portion of the unit cell of the structure of bis(cyclohexylbenzene)silver perchlorate down the *b* axis. The silver is coordinated to two aromatic rings and to O(1) in the cell above that pictured.

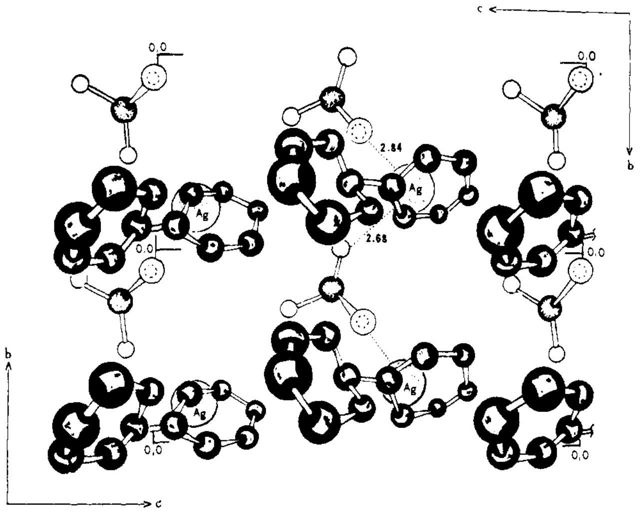

Figure 2. A perspective view down the *a* axis of bis(cyclohexylbenzene)silver perchlorate showing one $AgClO_4$ layer and one hydrocarbon layer.

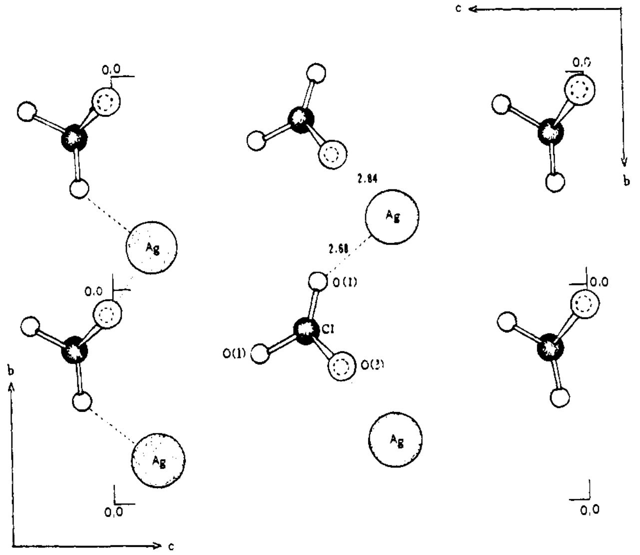

Figure 3. A perspective view down the *a* axis of bis(cyclohexylbenzene)silver perchlorate showing one $AgClO_4$ layer and the weak Ag–O interactions which produce a chain-like structure. The Ag, Cl, O(1), and O(2) lie in a crystallographic mirror, while O(3), which is represented by the solid circle, and O(3′), which is represented by the dotted circle, are symmetry related through the mirror.

aromatic, or anion present. In this structure the asymmetry is reflected both in the distances [Ag–C(6), 2.48 (1) Å; Ag–C(1), 2.66 (1) Å] and in the angles [Ag–C(1)–C(6), 66 (1)°; Ag–C(6)–C (1), 82 (1)°] associated with the C–C bond nearest the silver. This asymmetry may be characteristic not only of the silver(I)–aromatic interaction, but also of general metal(I)–aromatics since a similar situation of 2.15 (3) and 2.30 (3) Å is reported for Cu–C distances in the structure of C_6H_6–$CuAlCl_4$.[38,39] The second and longer Ag–C interaction varies over wide limits, 2.58–2.92 Å, and may well depend on a variety of factors such as molecular packing, nature of anion, electronegativity of aromatic, or other structural details. According to Mulliken's model,[5] the most favorable position for a silver ion is at the point of highest π-electron density, directly above one

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(38) R. W. Turner and E. L. Amma, *J. Amer. Chem. Soc.*, **85**, 4046 (1963).

(39) R. W. Turner and E. L. Amma, *ibid.*, **88**, 1877 (1966).

of the carbon atoms of the ring. Dewar[6] maintained that silver(I) could act not only as an electron acceptor, but also as a donor of electrons from a filled d orbital to an empty molecular orbital of the aromatic. If this "back-donation" interaction is of importance in the stabilization of the complex, the best overlap is achieved when the silver is located in the π cloud equidistant between two carbon atoms. Such a situation is observed only in the case of naphthalenetetrakis(silver perchlorate) tetrahydrate,[20] where the silver interaction with waters of hydration effect a perturbation upon the silver–aromatic interaction. However, since the asymmetric interaction occurs so often, it appears that "back-bonding" is the weaker of the two effects.

The angle of twist between the plane of the benzene ring and the plane defined by C(4)–C(7)–C(12) is 50 (1)°. Presumably, this twisted conformation minimizes nonbonded interactions between aromatic hydrogens and aliphatic hydrogens. The cyclohexyl portion of the hydrocarbon moiety is in the expected chair configuration with the junction to the benzene portion in the equatorial position. The bond distances and angles are normal within experimental error (Table II). Obviously, there would be nothing to gain energetically if the cyclohexyl group were to go into a boat configuration. Since the ring is so regular and the carbon temperature factors are exactly what might be expected, there is little possibility for chair–boat rearrangement, even in solution. This would indicate in turn that simple packing effects have little to do with the stabilization of the crystalline complex.

The aromatic ring is planar within experimental error, having a maximum deviation of 0.02 Å from the least-squares plane for the six atoms of the aromatic ring and the atom of the cyclohexyl moiety joining the ring (Table IV). Although the angles within the aromatic ring show little evidence of distortion (Table II), the bond distances seem to be systematically distorted toward an unconjugated cyclohexadiene-type structure. The C(2)–C(3) bond distance is 1.34 (2) Å and that of C(5)–C(6) is 1.38 (2) Å, while the remaining four distances of the ring average 1.43 (1) Å. Examination of the two halves of the ring described by the C(1)–C(4) diagonal (Figure 1) reveals a common long–short–long sequence in C–C distances, with only slightly more distortion in the half more closely associated with the silver ion. The difference in the long and short distances is six to seven deviations, and hence its statistical significance appears to be real. While this may indeed be evidence for some loss of aromatic character by the ring, there simply is not enough evidence either here or in the few similar systems known to explain completely the reason for the ring distortion. There is little evidence to suggest that the distortion is the result of packing or stereochemical effects.

It is interesting to observe that the nearest Ag–C interaction is at the meta position to the aliphatic substituent on the aromatic ring, rather than at the preferred para position for electrophilic attack. It is most likely that the reason for this unexpected position for interaction is stereochemical in origin due to the bulk of the cyclohexyl group. There is, however, no evidence for any nonbonded distance that is less than the expected van der Waals distance. It is also possible that the substitution position may be a result of as yet poorly understood electronic effects. This view is supported by an examination of the structure of bibenzylsilver perchlorate,[21] in which the silver is disordered such that it is associated with the meta position some 64% of the time and with the para position the rest of the time. Also to be considered is bis(*m*-xylene)silver perchlorate,[18] in which the shortest silver-to-carbon distance is at the anticipated ortho and para positions exclusively. A more detailed understanding of electron effects is not available at this time and requires further study.

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