$R < 2$ does not react with DBA. While the formation of $BH^+H_3X_4^-$ is not ruled out, no strong evidence for its existence exists.

The reaction of CHA and TCA was studied in the range $0 < R < 4$. CHA is slightly associated and the DVP data in Figure 3 suggest it forms a B_2HX adduct when CHA is in excess. This inference is drawn from the observation that the slope of the i *vs.* R curve is less than -1 at low values of R. At $R = 1$ both the DVP and infrared data indicate complete precipitation of a 1:1 adduct. The precipitate redissolves as more TCA is added, producing an increase in i between $R = 1$ and $R = 2$. The shape of the plot suggests that a species such as $(BHX)_nHX$ may form to a limited extent in addition to $BH^+HX_2^-$. The slope of the i *vs.* R plot, $3 < R < 4$, is 0.32, showing that TCA is still reacting with CHA. Changes in the infrared spectrum at 1244, 838, and 826 cm^{-1}, $2 < R < 3$, substantiate this conclusion.

An apparent discrepancy between the DVP and infrared data exists. The absorptions accredited to the carbonyl group at $R = 2$ and $R = 3$ are higher than the values that would be predicted from the DVP data. However, it seems likely that the carbonyl environment in the species $BH^+HX_2^-$ is very similar to the environment in $(HX)_2$ and thus could have an absorption maxium at about 1740 cm^{-1}. The peaks observed at $\sim$1740 cm^{-1}, for R values of 2 and 3, are much broader than in the pure acid.

The reaction between TBA and TCA is somewhat surprising. As seen from the i *vs.* R curve in Figure 3, one molecule of TBA can react quantitatively with four molecules of TCA, a result which is unexpected for a base as large as TBA. The first compound is an insoluble 1:1 adduct. The early rounding in the i *vs.* R plot indicates the conversion of insoluble $B \cdot HX$ to slightly soluble $B \cdot 2HX$ well before $R = 1$. Slightly soluble $B \cdot 3HX$ and $B \cdot 4HX$ appear to be forming since, as shown in Table I, a large excess of acid is required to dissolve the precipitate which formed initially. Weak infrared absorptions are seen in TBA–TCA solutions at $R = 2$ and $R = 3$. Infrared spectra at $R = 4$, 5, and 6 show that TCA is still adding a nonquantitative manner to form higher adducts.

Conclusion

Trichloacetic and benzoic acids react with a number of organic amines to form associated, uncharged ionic aggregates. Depending upon the reacting acid and base, the associated species include the simple ion pair, the homoconjugate ion pair, and ion pairs consisting of the protonated amine and more complex homoconjugate ions carrying a single negative charge. Evidence for species with a stoichiometry B_kHX ($k > 1$) is given. Association of aggregates is considerably greater in hexane than in benzene.

Acknowledgment. This work was supported in part by the National Science Foundation through its undergraduate research participation program in the Chemistry Department of the University of Minnesota, Minneapolis, and its research grant program.

Metal Ion–Aromatic Complexes. VII. The Crystal and Molecular Structure of Bis(*m*-xylene)silver Perchlorate

I. F. Taylor, Jr., E. A. Hall, and E. L. Amma[1]

Contribution from the Department of Chemistry, University of South Carolina,
Columbia, South Carolina 29208. Received March 6, 1969

Abstract: The crystal and molecular structure of bis(*m*-xylene)silver(I) perchlorate has been determined by single-crystal X-ray diffraction from 672 counter intensities measured at ambient temperature. The crystals were found to be orthorhombic: $a = 16.594$ (8) Å, $b = 8.861$ (5) Å, $c = 5.795$ (3) Å; space group $P2_12 2_1$. The structure was refined by full-matrix least squares to a final conventional R factor of 0.050. The structure may be described as alternating tetrahedra of ClO_4^- ions and four coordinate Ag(I) sharing an oxygen vertex. The coordination tetrahedron of Ag(I) is composed of the two Ag–O interactions and two bonds to the π electrons of *m*-xylene rings. This tetrahedron is very flattened with an Ag–O distance of 2.49 ± 0.01 Å and O–Ag–O angle of 125.0 ± 0.8° together with an Ag–C distance of 2.45 ± 0.02 Å and C–Ag–C′ angle of 161.7 ± 0.8°. The next shortest Ag–C distance is 2.61 ± 0.02 Å. Hence, the Ag(I) is asymmetrically located relative to the nearest C–C bond of the aromatic ring. The shortest Ag–C distance is *ortho* and *para* to the methyl ring substituents. The aromatic moiety is normal within experimental error. It is clear that the perchlorate group plays a significant role in stabilizing this metal ion–aromatic complex.

The existence of donor–acceptor complexes between aromatic moieties and Ag(I) has been known for some time.[2-4] The 1:1 complexes are well known and the crystal structures of $C_6H_6 \cdot AgClO_4$[5] and $C_6H_6 \cdot AgAlCl_4$[6] have been determined. The former has been shown to be a polymeric complex and the latter a 1:1 complex with a five-coordinate Ag(I) entity. However, solution evidence,[2-7] composition phase diagrams,[8] and

---

[1] Address all correspondence to this author.

[2] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **71**, 3644 (1949).

[3] L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 3113 (1950).

[4] L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 5034 (1950).

[5] H. G. Smith and R. E. Rundle, *ibid.*, **80**, 5075 (1958).

[6] R. W. Turner and E. L. Amma, *ibid.*, **88**, 3243 (1966).

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

Atom	x	y	z	Atom	x	y	z
Ag	0.0000 (—)	0.0274 (02)	0.0000 (1)	C(5)	0.0943 (10)	0.3702 (24)	−0.2610 (30)
Cl	0.0000 (—)	−0.0191 (05)	0.5000 (—)	C(6)	0.0902 (11)	0.5148 (26)	−0.1671 (32)
C(1)	0.1314 (10)	0.5378 (20)	0.0488 (40)	C(11)	0.1316 (12)	0.6991 (23)	0.1567 (42)
C(2)	0.1776 (10)	0.4320 (22)	0.1584 (30)	C(33)	0.2252 (12)	0.1545 (24)	0.1691 (42)
C(3)	0.1774 (09)	0.2782 (21)	0.0539 (22)	O(1)	0.0475 (07)	0.0775 (17)	0.3570 (24)
C(4)	0.1344 (10)	0.2512 (20)	−0.1610 (33)	O(2)	0.0549 (08)	−0.1119 (16)	0.6294 (24)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag	0.0038 (00)	0.0164 (03)	0.0357 (06)	0.0000 (—)	0.0025 (04)	0.0000 (—)
Cl	0.0037 (02)	0.0117 (07)	0.0250 (14)	0.0000 (—)	−0.0011 (13)	0.0000 (—)
C(1)	0.0036 (06)	0.0140 (24)	0.0467 (125)	0.0009 (11)	0.0011 (22)	−0.0117 (46)
C(2)	0.0035 (06)	0.0197 (33)	0.0281 (56)	0.0003 (13)	0.0003 (17)	−0.0033 (41)
C(3)	0.0038 (06)	0.0148 (24)	0.0204 (70)	0.0016 (11)	0.0014 (14)	0.0029 (32)
C(4)	0.0041 (07)	0.0169 (33)	0.0346 (65)	−0.0007 (13)	0.0039 (20)	−0.0038 (39)
C(5)	0.0035 (07)	0.0239 (41)	0.0271 (59)	−0.0018 (14)	−0.0023 (18)	0.0014 (43)
C(6)	0.0038 (07)	0.0252 (43)	0.0276 (65)	0.0006 (15)	0.0002 (20)	0.0009 (46)
C(11)	0.0071 (11)	0.0161 (29)	0.0690 (104)	−0.0016 (17)	0.0051 (30)	−0.0172 (57)
C(33)	0.0054 (09)	0.0207 (36)	0.0687 (106)	0.0033 (15)	−0.0054 (30)	0.0071 (59)
O(1)	0.0052 (06)	0.0258 (27)	0.0601 (61)	−0.0017 (10)	0.0052 (17)	0.0228 (36)
O(2)	0.0070 (07)	0.0242 (25)	0.0536 (57)	0.0065 (11)	−0.0040 (18)	0.0126 (35)

Scale Factor = 0.823 (4)

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

temperature composition diagrams[9] have indicated aromatic-to-silver ratios different from 1:1. The properties of one such compound, (cyclohexylbenzene)$_2$Ag-ClO$_4$, have been reported along with the crystal structure.[10] In addition we have isolated the following crystalline complexes: (m-xylene)$_2$AgClO$_4$, naphthalene·4AgClO$_4$·4H$_2$O, (p-xylene)$_2$AgClO$_4$, bibenzyl·AgClO$_4$, anthracene·4AgClO$_4$·H$_2$O, (o-xylene)$_2$·AgClO$_4$, (s-mesitylene)$_2$·AgClO$_4$, and acenaphthene·AgClO$_4$. We wish to report here on the results of the structure analysis of the first of these; the other analyses are in process.

The nature of the bonding between Ag(I) and aromatics has been discussed by Mulliken[11] and Dewar,[12] and molecular orbital calculations[13] have been made to predict the positioning of the silver ion in substituted benzenes and other aromatics. From our systematic study of the structures, we believe that we can get a better fundamental understanding of the matter, sorting out the important effects—steric, electronic, molecular-packing, or whatever else.

Experimental Section

Anhydrous silver perchlorate was dissolved in m-xylene, and m-xylene was slowly removed in an anhydrous environment. As the solution became more concentrated, seed crystals were added to initiate crystallization. By this means sufficient crystalline material for chemical analysis [*Anal.* Calcd for (m-xylene)$_2$·AgClO$_4$; Ag, 25.0. Found: Ag, 25.7] and good single crystals for diffraction studies were isolated. The colorless crystals, which are unstable in air both to decomposition by water vapor and to loss of aromatic, were sealed in thin-walled glass capillaries. Some decomposition occurred, nevertheless, and the crystals were always coated with a thin layer of "oil" from decomposition. No doubt this places some limitations on our intensity data. The crystals were aligned with the "c" axis approximately parallel to the capillary axis and to the axis of the goniometer head. Preliminary Weissenberg and precession photographic data $hk0$, $hk1$, . . ., $hk7$, $h0l$, $0kl$, showed the crystals to be orthorhombic, with the systematic absences $h = 2n + 1$ for $h00$, and $l = 2n + 1$ for $00l$, uniquely determining the space group as $P2_12_12_1$.[14] The crystal was aligned on the Picker diffractometer by variations of well-known techniques and the cell dimensions (λ 0.71068 Å for Mo Kα) are a = 16.594 (8), b = 8.861 (5), and c = 5.795 (3) Å. With $Z = 2$ the calulated density is 1.64 g cm^{-3} and the observed density is between 1.6 and 1.8 g cm^{-3}. A more accurate value was unattainable since the aromatic was rapidly stripped off by the solutions. A crystal ~0.2 × 0.2 × 0.5 mm mounted with the needle axis as above was used to collect the intensity data. Since μ = 13.3 cm^{-1} for Mo Kα and since errors in intensity measurements due to decomposition probably outweigh simple absorption effects, no absorption corrections were made. A total of 1800 independent hkl reflections were measured by the θ–2θ scan technique with Zr-filtered Mo Kα radiation at room temperature for 60 sec at 0.033°/sec and background counts were made for 20 sec (B_1 and B_2) at ±1.0° 2θ of peak maximum. $I(\text{net}) = I(\text{sum}) - 1.5(B_1 + B_2)$. Reflections were considered absent if the integrated intensity was less than twice the estimated σ of the background $[1.5(B_1 + B_2)^{1/2}]$; 672 nonzero intensities were retained by this criterion. A standard reflection was measured every tenth reflection to ensure stability of operation and to monitor any crystal decomposition. The total variation in the standard peak during data collection was less than 6% of the net intensity (~10,000) or within four standard deviations of I(net). $\sigma[I(\text{net})] = [I(\text{sum}) + (1.5)^2(B_1 + B_2)]^{1/2}$. In general, the variation from one measurement of the standard peak to the next was one-half of a standard deviation or less. The take-off angle, source-to-crystal distance, and crystal-to-counter distance were 3.7°, 18 cm, and 23 cm, respectively. 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 0.2° at the 3.7° take-off angle indicating a mosaic spread such that all the reflection is counted during the scan. This 0.2° is not an absolute value since the total mosaic spread depends upon other instrumental factors as well. The counting rate never exceeded 5000 counts/sec, and no attenuators were used. Lorentz–polarization corrections were made to reduce the intensities to relative structure factors.

Solution of Structure

With two (m-xylene)$_2$·AgClO$_4$ formula weights per cell the Ag and Cl atoms are required to lie on crystallographic twofold axes of $P2_12_12_1$, *i.e.*, $0, y, {}^1/_2$; ${}^1/_2, \bar{y}, 0$ or $0, y, 0$; ${}^1/_2, \bar{y}, {}^1/_2$. The oxygen atoms of the perchlo-

---

(7) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **74**, 640 (1952).

(8) B. G. Torre-Mori, D. Janjic, and B. P. Susz, *Helv. Chem. Acta*, **47**, 1172 (1964).

(9) G. Peyronel, G. Belmondi, and I. M. Vezzosi, *J. Inorg. Nucl. Chem.*, **8**, 577 (1958).

(10) E. A. Hall and E. L. Amma, *Chem. Commun.*, 622 (1968).

(11) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

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

(13) K. Fukui, A. Imamura, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Japan*, **34**, 1076 (1961).

(14) "International Tables for X-Ray Crystallography," Vol. I, N. F. M. Henry and K. Lonsdale, Ed., The Kynoch Press, Birmingham, England, 1952, pp 104, 546.

rate group and the carbon atoms of the aromatic moiety are in the general positions: x, y, z; $\bar{x}, y, \bar{z}$; $\frac{1}{2} + x, y, \frac{1}{2} - z$; $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$. A three-dimensional Patterson map[15] readily yielded the y coordinates of the Ag and Cl atoms. A structure-factor calculation based upon these atoms yielded an R factor of 0.36. A three-dimensional Fourier map was computed with phases based upon these two atoms; it located the remaining atoms. Three cycles of full-matrix isotropic least squares[16] reduced R to 0.15. A three-dimensional difference Fourier map indicated appreciable anisotropic thermal motions of the atoms. Five cycles of full-matrix anisotropic least squares yielded 0.050, 0.065, and 1.56 for R, the weighted R, and the standard error of an observation of unit weight.[17] The final parameter shifts were 0.1σ or less.

The function minimized was $\Sigma w(F_o - F_c)^2$ with unit weights. The scattering factors for Ag(I), neutral chlorine, oxygen, and carbon were from Cromer and Waber.[18] The effects of anomalous dispersion were included in the structure factor calculations by addition to F_c;[19] the values for $\Delta f'$ and $\Delta f''$ for Ag(I) were those given by Cromer.[20] The final tabulation of observed and calculated structure factors is available to those interested.[21] Absent reflections were not used in the structure refinement and are not included in the table. Final atomic positional and thermal parameters are listed in Table I. Interatomic distances and angles, root-mean-square components of thermal displacement, dihedral angles between normals to planes, and their errors were computed[22] with the parameters and variance–covariance matrix from the last cycle of least-squares refinement and are listed in Table II. The least-squares plane $Ax + By + Cz + D = 0$ for the benzene ring has $A = 0.8192$, $B = 0.2568$, $C = 0.5128$, and $D = -2.8868$ Å. The maximum deviation from this plane is 0.027 (15) Å (including methyl carbons). Hence, all carbon atoms lie in the same plane[23] well within experimental error.

To check that our results were not an artifact of a particular weighting scheme, we also refined on F^2 with unit weights, F^2 with variable weights, and F with variable weights.[24] All gave essentially the same results except for the rms amplitudes of thermal motion which seems more reasonable for the refinement reported above. A final difference map was qualitatively flat and showed no unexpected features.

Table II

	Bond Lengths, Å		
Ag–C(4)	2.45 (02)	C(1)–C(6)	1.44 (03)
Ag–C(5)	2.61 (02)	C(1)–C(2)	1.42 (03)
		C(2)–C(3)	1.42 (02)
Ag–O(1)	2.49 (01)	C(3)–C(4)	1.45 (02)
		C(4)–C(5)	1.37 (02)
Cl–O(1)	1.43 (01)	C(5)–C(6)	1.39 (03)
Cl–O(2)	1.44 (01)	C(1)–C(11)	1.56 (02)
		C(3)–C(33)	1.51 (02)
	Nonbonded Distances less than 4 Å[a]		
Ag–Cl	3.52 (00)	C(2)–O(1)	3.92 (02)
		C(3)–O(1)	3.30 (02)
Ag–C(1)	3.66 (02)	C(4)–O(1)	3.67 (02)
Ag-C(2)	3.63 (02)	C(4)–O(1)′	3.57 (02)
Ag–C(3)	3.03 (02)	C(4)–O(1)″	3.50 (02)
Ag-C(6)	3.25 (02)	C(5)–O(1)′	3.54 (02)
Ag–C(33)	3.89 (02)	C(5)–O(1)″	3.50 (03)
		C(11)″–O(1)	3.81 (02)
Ag–O(1)″	3.98 (02)	C(33)–O(1)	3.22 (02)
Ag–O(2)″	3.67 (01)		
		C(4)–O(2)″	3.68 (02)
Cl-C(4)′	3.82 (02)	C(11)″–O(2)	3.45 (02)
Cl-C(5)′	4.03 (02)	C(33)–O(2)‴	3.68 (02)
Cl–C(11)″	3.87 (02)		
		C(6)–C(6)′	3.56 (04)
O(1)–O(2)	2.31 (02)		
	Angles, Deg		
C(1)–C(2)–C(3)	117.1 (15)	C(2)–C(3)–C(33)	117.9 (15)
C(2)–C(3)–C(4)	121.0 (16)	C(2)–C(1)–C(11)	118.4 (17)
C(3)–C(4)–C(5)	118.2 (17)	C(1)–C(4)–Ag	87.9 (06)
C(4)–C(5)–C(6)	124.3 (17)	C(2)–C(5)–Ag	83.5 (06)
C(5)–C(6)–C(1)	116.5 (19)	C(4)–Ag-C(5)	31.3 (05)
C(2)–C(1)–C(6)	122.8 (18)	C(4)–Ag-C(4)′	161.7 (08)
		C(5)–C(4)–Ag	80.9 (05)
O(1)–Cl–O(1)′	125.5 (06)	C(4)–C(5)–Ag	67.8 (05)
O(2)–Cl–O(2)′	121.9 (07)		
O(1)–Cl–O(2)	107.2 (08)	Ag–O(1)–Cl	125.7 (07)
		O(1)–Ag–O(1)‴	125.0 (07)
Ag–Cl–O(1)	35.1 (05)	Ag–C(4)–O(1)	42.6 (03)
Ag–Cl–O(2)	139.0 (06)	C(4)–Ag–O(1)	95.8 (05)
Cl–Ag–Cl′	110.6 (01)	C(2)–C(5)′–C(2)′	110.7 (06)

Root-Mean-Square Displacements along Principal Axes of Thermal Ellipsoid, Å

Atom	Axis 1	Axis 2	Axis 3
Ag	0.209 (04)	0.255 (02)	0.263 (04)
Cl	0.200 (12)	0.216 (06)	0.233 (11)
C(1)	0.176 (28)	0.234 (20)	0.317 (35)
C(2)	0.213 (24)	0.221 (21)	0.284 (24)
C(3)	0.178 (32)	0.210 (21)	0.267 (21)
C(4)	0.197 (24)	0.247 (26)	0.290 (25)
C(5)	0.188 (25)	0.234 (25)	0.315 (26)
C(6)	0.216 (26)	0.228 (23)	0.317 (27)
C(11)	0.196 (30)	0.292 (24)	0.395 (30)
C(33)	0.201 (28)	0.322 (26)	0.361 (28)
O(1)	0.164 (22)	0.295 (17)	0.403 (18)
O(2)	0.164 (22)	0.333 (18)	0.384 (17)

[a] A single prime means related by twofold symmetry axis; double prime, related by translational symmetry; triple prime, related by translational symmetry plus twofold axis in the y direction to unprimed atoms.

---

(15) Patterson and electron density syntheses were calculated using "ERFR-3, A Three Dimensional Fourier Summation Program Adapted for the IBM 7040 from ERFR-2 of Sly, Shoemaker, Van den Hende," by D. R. Harris.

(16) Structure factor calculations and least-squares refinements were performed with a local version of 'ORFLS, A Fortran Crystallographic Least Squares Program," by W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, Oak Ridge, Tenn., ORNL-TM-305, 1962.

(17) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; weighted $R = [\Sigma w[|F_o| - |F_c|^2]^{1/2}/[\Sigma w|F_o|^2]^{1/2}$; std error $= [\Sigma w(F_o - F_c)^2/\mathrm{NO} - \mathrm{NV}]^{1/2}$; NO = 672, NV = 101.

(18) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18,** 104 (1965).

(19) J. A. Ibers and W. C. Hamilton, *ibid.*, **17,** 781 (1964).

(20) D. T. Cromer, *ibid.*, **18,** 17 (1965).

(21) These tables have been deposited as Document No. NAPS-00491 with the ASIS National Auxiliary Publication Service, ℅ CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

(22) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(23) Local program for least-squares plane for the IBM 1620 due to W. A. Spofford, III. x, y, z refers to an internal orthogonal coordinate system; see J. S. Rollett, "Computing Methods in Crystallography," Pergamon Press, New York, N. Y., 1965, p 22; esd's of individual atoms were used as weights.

(24) S. W. Peterson and H. A. Levy, *Acta Cryst.*, **10,** 70 (1957).

$$w = 1/\sigma^2$$

$$\sigma^2(F^2) = S/(\mathrm{Lp})^2[I(\mathrm{scan}) + (1.5)^2(B_1 + B^2) + (0.04I(\mathrm{scan}))^2]$$

$$\sigma^2(F) = \frac{S}{\mathrm{Lp}} \cdot \frac{1}{F}[I(\mathrm{scan}) + (1.5)^2(B_1 + B_2) + (0.04I(\mathrm{scan}))^2]^{1/2}$$

where S = a scale factor and Lp is the Lorentz–polarization factor and the other terms as defined above.

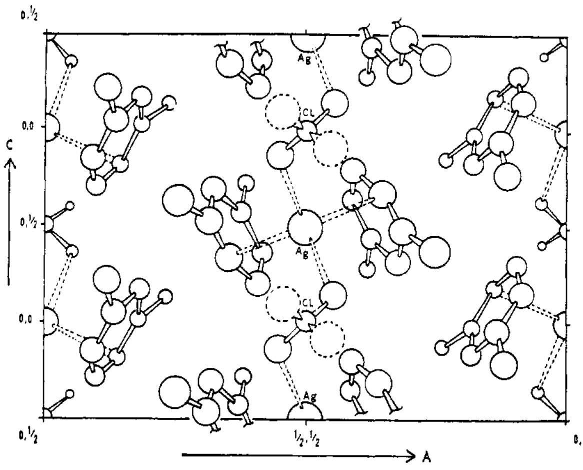

Figure 1. A perspective view of the $(m\text{-xylene})_2 \cdot AgClO_4$ structure down the *b* axis. The Ag and Cl atoms lie on crystallographic twofold axes normal to the plane of the paper. The distorted tetrahedral arrangement about Ag is made up of oxygens from two ClO_4^- ions and carbons from two *m*-xylene molecules.

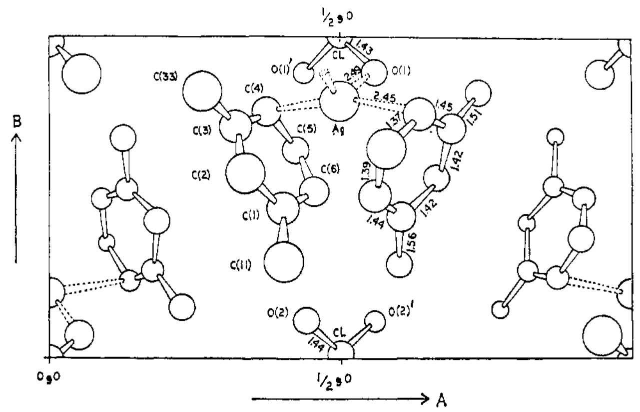

Figure 2. A perspective view of the $(m\text{-xylene})_2 \cdot AgClO_4$ structure down the *c* axis. The $AgClO_4$ "sheet" is at *a*/2, and the $AgClO_4$ chain propagates normal to the plane of the paper.

Results and Discussion

The gross features of the structure can be described in terms of parallel sheets of "ionic" matter ($AgClO_4$) separated by sheets of "insulation," the organic groups (Figures 1 and 2). The $AgClO_4$ sheets are made up of $-Ag-OClO_2O-Ag$ chains which are only weakly bonded together. The Ag is then further bonded to the π orbitals of *m*-xylene groups on opposite sides of the sheet or chains. The net result is that the structure may be viewed as alternating tetrahedral of ClO_4^- ions and four coordinate Ag(I) sharing a common oxygen vertex. The coordination of Ag is made up of oxygen atoms from two different ClO_4^- tetrahedra and two carbon atoms from the aromatic donors (Figures 1 and 2 and Table III). Crystallographically the Ag and Cl atoms lie on twofold axes of $P2_12 2_1$.

Table III. Ag–C Distances in a Variety of Ag–Ar Complexes

Compound	Ag–C, Å	Ag–C′, Å	Δ, Å
Bibenzyl · $AgClO_4$[a,b]	2.48 (2)	2.72 (2)	0.24
(cyclohexylbenzene)$_2$ · $AgClO_4$[c]	2.48 (1)	2.67 (1)	0.19
Benzene · $AgClO_4$[b,d]	2.496 (6)	2.634 (6)	0.142
Benzene · $AgAlCl_4$[e]	2.47 (6)	2.92 (7)	0.45
Anthracene · $4AgClO_4 \cdot H_2O$[f]	2.48, 2.45	2.55, 2.56	0.07, 0.11
(*m*-xylene)$_2$ · $AgClO_4$[g]	2.45 (2)	2.61 (2)	0.15

[a] I. F. Taylor and E. L. Amma, submitted for publication. [b] Results somewhat complicated by disorder. [c] Reference 10. [d] Reference 5. [e] Reference 6. [f] E. A. Hall and E. A. Amma, submitted for publication. [g] This work.

The silver ion tetrahedron is very distorted from the ideal. The Ag–C distance is 2.45 (2) Å with an attendent C–Ag–C′ angle of 161.7 (8)°. The Ag–O distance is 2.49 (1) Å with a concomitant O–Ag–O′ angle of 125.0 (7)°. However, the dihedral angle between the planes defined by C(4)–Ag–C(4)′ and O(1)–Ag–O(1)′ is 88.2 (6)°. Hence, the tetrahedron is flattened but not twisted. These Ag–O interactions seem to be much more important in stabilizing the structure than in previously reported Ar · $AgClO_4$ complexes, where the shortest distances were ~2.66 Å.[4,5] The Ag–O single bond radius sum is 2.18 Å.[25] As expected under these conditions the O–Cl–O angle of the ClO_4^- opens up from the idealized 109 to 125.5 (6)°. However, the Cl–O distances seem to be normal for a ClO_4^- ion.

The aromatic entity is not significantly different from what would be expected for the uncomplexed molecule. It is interesting to note that the carbon atom closest to the Ag is *ortho* and *para* to the methyl groups which would be the point of highest π electron density in the *m*-xylene unit. However, this naive point of view does not hold for other compounds in the series, *e.g.*, bis(cyclohexylbenzene)silver perchlorate.

Table III shows that a Ag–C distance of 2.47 ± 0.02 Å is a common feature of all known structures of Ag(I) with aromatic molecules, regardless of stereochemistry, nature of aromatic, or anion present. However, the next longest distance (Ag–C′) varies over rather wide limits, 2.58–2.92 Å. Under these circumstances the conclusion seems inescapable that the dominant interaction between the Ag and the aromatic is with this nearest carbon atom, and the other Ag–C distance may depend upon a number of other factors such as molecular packing, nature of anion, and other structural details.

It is to be noted that in the structure reported herein the C(5)–C(4)–Ag angle of 80.9 (5)° is considerably different from the C(4)–C(5)–Ag angle of 67.8 (5)°, further reflecting the asymmetry of the Ag position.

The 2.45- and 2.61-Å Ag–C distances deserve some comment. If the metal behaves as an electron acceptor from the aromatic, then regardless of whether the metal acceptor orbital is 5s, 5p, or some mixture thereof, the best position for the metal ion would be in the π cloud above one of the carbon atoms of the ring, the position of highest π electron density. On the other hand, if back-donation metal → aromatic is important, then the best overlap between the filled metal d orbitals and the antibonding π MO of the aromatic moiety is achieved with the metal in the π cloud equidistant between two carbon atoms of the ring. In the general case some compromise should be reached. It appears from the results shown in Table I that if one of these two interactions is to yield to packing or other such small forces the back-donation interaction bears the cost since the shortest Ag–C distance is invariant at 2.47 Å.

---

(25) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

In contrast to this fixed Ag–C distance of 2.47 Å in Ag–aromatic complexes, the shortest Ag–C distance in olefin complexes varies over a considerable range,[26–31] from a short 2.31 (4) Å in norbornadiene·$2AgNO_3$[26] to 2.45 Å in the 3:1 bullvalene·$AgNO_3$ complex.[30]

Acknowledgment We wish to acknowledgment financial support from NSF Grant GP-6747.

---

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

[27] F. S. Mathews and W. N. Lipscomb, *J. Phys. Chem.*, **63**, 845 (1959).

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

[29] J. S. McKechnie and I. C. Paul, *J. Chem. Soc.*, *B*, 1445 (1968).

[30] J. S. McKechnie, M. G. Newton, and I. C. Paul, *J. Am. Chem. Soc.*, **89**, 4819 (1967).

[31] R. B. Jackson and W. E. Streib, *ibid.*, **89**, 2539 (1967).

The Crystal Structure of the Chlorine Complex of Bis(*p*-chlorophenyl) Sulfide

N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson

Contribution from the Department of Chemistry, The University of Iowa, Iowa City, Iowa 52240. *Received December 20, 1968*

Abstract: The crystal structure of a chlorine complex of bis(*p*-chlorophenyl) sulfide was determined from single-crystal Weissenberg and precession X-ray diffraction patterns from a crystal maintained at 143°K. The cell dimensions at that temperature are $a = 12.876 \pm 0.003$ Å, $b = 7.795 \pm 0.002$ Å, $c = 13.794 \pm 0.004$ Å, $\beta = 111.02 \pm 0.03°$, space group $P2_1/c$; four molecules of $(ClC_6H_4)_2SCl_2$ per cell give a calculated density of 1.796 g/cm^3. Visual estimates of the 1213 observed reflections were fitted by least-squares methods to give an R of 0.11. The structure of the complex may be described as a trigonal bipyramid about sulfur with the *p*-chlorophenyl groups and an unshared pair of electrons occupying the equatorial plane (C–S–C bond angle = 109°), and the Cl atoms occupying axial positions at 2.26 and 2.32 Å. The trigonal-bipyramid groups align themselves into long chains with the Cl–Cl distances between groups being 3.31 Å. The intermolecular interactions are nearly linear (Cl–S–Cl···Cl–S–Cl···; Cl···Cl–S angle is 162°). The configuration of the complex fits logically into the series of observed group VI–group VII complexes.

Recently, an investigation was begun to seek a new and purer synthetic route from organic sulfide compounds to the organic sulfoxide derivatives. In an intermediate step in the procedure involving halogenation of organic sulfides, solid complexes were found. The chlorine complex of bis(*p*-chlorophenyl) sulfide was one of the most stable of the products observed. Nmr work indicated that the complexing chlorine atoms were symmetrically disposed with respect to the organic portion of the molecule.[1] These studies together with the structures of reported group VI–halogen complexes indicated very strongly that there would be a trigonal-bipyramidal configuration about the sulfur atom. The single-crystal structural analysis was undertaken to verify this prediction and to determine if the bond distances would correspond to the labile chemical character of the complex.

Experimental Details

The crystals used in the investigation of the chlorine complex of bis(*p*-chlorophenyl) sulfide, $C_{12}H_8Cl_4S$, were prepared by the gaseous chlorine saturation of an ice-cold carbon tetrachloride solution of the diaryl sulfide, as described by Maner.[2] Product identification was confirmed *via* ir and nmr spectral and chemical analysis.

The crystals formed were quite unstable even under solution, being decomposed by traces of moisture and by lowering the partial pressure of chlorine. Because of these difficulties individual crystals were mounted in glass capillaries and stored under liquid nitrogen, and the X-ray diagrams were made with the crystals maintained at ~143°K. The cell dimensions were obtained from Weissenberg camera back-reflection photographs at low temperature. A least-squares treatment of the film coordinates of observable reflections gave the following cell dimensions: $a = 12.876 \pm 0.003$ Å, $b = 7.795 \pm 0.002$ Å, $c = 13.794 \pm 0.004$ Å, and $\beta = 111.02 \pm 0.03°$. The systematic absences of l odd in ($h0l$) data and of k odd in ($0k0$) data indicated the space group as $P2_1/c$.

Film intensity data were gathered for layers ($hk0$) through ($hk7$) using multiple-film equiinclination Weissenberg low-temperature techniques with Cu Kα radiation (1.5418 Å, Ni filter). The crystal used was twinned in such a fashion that reflections from the twinned portions exactly superimposed only in layers ($hk3$) and ($hk6$) (twin axis = [001]). These data were discarded. The twinned reflections were separately indexed in the remaining layers and the intensity data were utilized. Additional film intensity data taken at low temperature were obtained for layers ($0kl$) through ($5kl$) and for layers ($h0l$) through ($h3l$) utilizing Buerger precession camera techniques with Mo Kα radiation (0.7107 Å, Zr filter). The precession data sets were obtained from single crystals which were obtained by cleaving the twinned crystals which always were found.

Because of the instability of the crystalline complex and the lack of a suitable displacement medium at near-normal temperatures, the density of the compound was not determined experimentally. The sulfide complex crystals were observed, however, to have a density slightly greater than that of the chlorine-saturated CCl_4 solution from which they were grown. It seemed reasonable to assume that the density of the chlorine gas saturated solution did not deviate greatly from the density of pure carbon tetrachloride (1.594 g/ml).[3] A calculated density value of 1.796 for four molecules of $(ClC_6H_4)_2SCl_2$ per unit cell is quite compatible with the rough specific gravity observation.

The accumulated intensity data were multiply estimated by visual means. The estimates obtained for a given reflection and its sym-

---

[1] R. E. Buckles and R. J. Maner, submitted for publication.

[2] R. J. Maner, Ph.D. Dissertation, University of Iowa, 1967.

[3] "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1968, p C-407.