Low-Temperature Neutron Diffraction Study of the Silver Perchlorate–Benzene π Complex†

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Abstract

The crystal structure of the $AgClO_4.C_6H_6$ π complex, earlier determined by X-ray diffraction at room temperature, has been redetermined at 18, 78 and 158 K by neutron diffraction. Crystal data: ortho-rhombic, space group *Cmcm*, $Z = 4$, $F(000) = 225.318$ fm, $T = 18$, 17, 158 K; $D_x = 2.591\,(2)$, 2.570 (1), 2.523 (1) g cm^{-1}; $\mu_n = 0.166$, 0.165, 0.162 cm^{-1}; $a = 7.913\,(1)$, 7.973 (1), 8.100 (1), 8.336 (1) Å (at 295 K); $b = 7.837\,(2)$, 7.857 (1), 7.902 (1), 7.996 (1) Å (at 295 K); $c = 11.798\,(3)$, 11.777 (2), 11.739 (2), 11.638 (2) Å (at 295 K); $wR(F^2) = 0.037$, 0.035, 0.045, $S = 1.18$, 1.08, 1.10 for 782, 628, 800 reflections and 51 variable parameters. This study confirms the principal features reported in the X-ray investigation and reveals details of structure not observable at room temperature. Distortions of the benzene molecule from D_{6h} symmetry ascribed to $Ag^+\cdots C_6H_6$ interactions are small, but significant. At 18 K the two C—C bonds complexed by Ag^+ are 1.405 (1) Å in length; the other four are 1.398 (1) Å. The C—H bonds are equal in length at 1.087 (2) (two) and 1.089 (1) Å (four). The H atoms nearest to Ag^+ are displaced 0.064 (1) Å from the C_6 plane, away from the silver. The shortest $Ag^+\cdots C$ distance of the complex is 2.565 (1) Å. This value and bond lengths of the benzene molecule are invariant between 18 and 158 K within 2 e.s.d.'s or less. The nonequivalent bond lengths of ClO_4^-, 1.451 (1) (two) and 1.441 (1) Å (two) at 18 K, are foreshortened by -0.007 and -0.005 Å at 158 K by effects of thermal motion. The O—Cl—O angles, 109.08 (7), 109.98 (2) and 107.83 (8)° at 18 K, are virtually unchanged by temperature. The $Ag^+\cdots ClO_4^-$ interactions occur at $Ag^+\cdots O$ distances of 2.785 (1) and 2.612 (1) Å (18 K), where the shorter values involve ClO_4^- acting as a bidentate group. Rigid-body and riding-motion models do not adequately account for the observed temperature dependence of bond lengths in ClO_4^- nor provide significant corrections to the C_6H_6 bond lengths at 18, 78 and 158 K beyond their uncertainty limits. A harmonic potential rationalizes the motion of Ag^+ at these three temperatures.

1. Introduction

Complexes of Ag(I) with π systems have been extensively studied by X-ray diffraction (Smith & Rundle, 1958; Mathews & Lipscomb, 1959; Baenziger, Haight, Alexander & Doyle, 1966;‡ Jackson & Streib, 1967; McKechnie & Paul, 1968; Taylor, Hall & Amma, 1969; Hall & Amma, 1969; Rodesiler, Griffith & Amma, 1972), subsequent to Mulliken's (1952, and references therein) proposal of the charge-transfer model to rationalize their stability. In the first such study, that of $AgClO_4.C_6H_6$, Smith & Rundle (1958) reported that the C—C bonds complexed to silver were shortened to 1.354 (17) Å, while the others were lengthened to 1.427 (10) Å with C—C—C angles of 115.7 and 122.3°. This structure analysis was rendered more difficult than usual by the occurrence of disorder or pronounced anisotropic thermal motion of Ag^+ and ClO_4^- ions and the uncertainty of choice among space groups, *Cmcm*, *Cmc2*₁ and *C2Cm*, indicated by systematic absences. The distortions in benzene geometry were questioned when it was discovered (Gilson & McDowell, 1964) that the NMR spectra are in accord with rapid benzene reorientation in the solid at room temperature, the temperature at which the X-ray study was undertaken. Smith (1964) in reply noted that X-ray density maps are consistent with highly hindered but not free benzene rotation, that the apparent distortions are approximately 3σ, or the commonly accepted limit of reliable measurement, and that X-ray diffraction is inherently limited in its ability to locate light atoms when a heavy atom such as silver is also present.

We have undertaken the present neutron diffraction study of the $AgClO_4.C_6H_6$ complex at 18, 78 and 158 K in an effort to provide definitive answers to questions remaining about the structure and, in particular, to distinguish between static and dynamic disorder, to

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‡ Marsh & Herbstein (1983) have reassigned the space group to *Cmcm* and refined the structure with original data.

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assess effects of thermal motion on bond lengths and interaction distances, and to obtain accurate molecular dimensions.

2. Experimental

Large crystals of $AgClO_4.C_6H_6$ were grown by slowly evaporating a solution of silver perchlorate in benzene. A colorless tablet weighing 9.26 mg, of approximate dimensions $1.0 \times 1.7 \times 2.0$ mm and bounded by large $\{001\}$ and smaller $\{110\}$ and $\{010\}$ faces, was mounted on an aluminum pin inside a 2 cm diameter silica-glass bulb. The neutron diffraction data were measured at the Brookhaven High Flux Beam Reactor on the four-circle diffractometer at beam port H6M and with a neutron wavelength of 1.046 Å, following procedures described in previous papers from this laboratory.* Measurements were made at 18, 78 and 158 K in order of increasing temperature. The lattice constants (Table 1), including values at 295 K, that are reported in the *Abstract* were determined by least-squares fits to $\sin^2 \theta$ data for 32 reflections with $44 < 2\theta < 56°$. Intensity data for reflections in a single octant, $0 \le h \le 12$, $0 \le k \le 12$, $0 \le l \le 18$, were collected by the $\omega/2\theta$ step scan method. Fixed scan widths of 3.2° were used below $\sin \theta/\lambda = 0.40$ Å^{-1}; beyond this value to $(\sin \theta/\lambda)_{max} = 0.77$ Å^{-1}, the widths were computed from the dispersion formula $\Delta 2\theta = 2.57 + 2.31 \tan \theta$. At least 65 points were sampled on each scan profile. Intensities of two reflections were remeasured at 3.5 h intervals and were found to be constant within 2% in each data set. Systematic absences (*hkl* with $h + k$ odd; *h0l* with l odd) of space groups *Cmcm*, *Cmc2₁* and *C2cm* were verified in the 18 K data set by scanning all reflections in the range $2 < 2\theta < 50°$ and all *h0l* reflections with $2\theta < 108°$. The integrated intensity of each reflection was evaluated from the scan data taking the two extreme 10% parts for estimates of background. The variance in intensity was derived from counting statistics. Lorentz and absorption corrections (Templeton & Templeton, 1973; de Meulenaer & Tompa, 1965) were applied and multiple observations, when present, were averaged to give the three data sets (Table 1) used in the refinements. Of these observations none were rejected, because of a large negative F_o^2 value; the number with $F_o^2 < -1\sigma(F_o^2)$ was 5, 3 and 9 in the 18, 78 and 158 K data sets, respectively. The absorption corrections applied corresponded to calculated transmission values ranging from 0.77 to 0.84, with a mean calculated transmission of 0.82.

The refinements were started with average atomic positions for non-H atoms derived from the X-ray study (Smith & Rundle, 1958) and assumed displacement parameters. Positions of H atoms were obtained from difference maps. Parameters of the model were refined with constraints of space group *Cmcm* against the three data sets and with constraints of space groups *C2cm* and *Cmc2₁* against the 18 and 158 K data. For the latter refinements, the initial atomic positions were arbitrarily shifted from their centrosymmetric *Cmcm* values by ~ 0.4 Å and in each refinement the parameters were first readjusted by differential Fourier synthesis. The final refinements were carried out by full-matrix least-squares, minimizing the quantity $\Sigma w|F_o^2 - (kF_c)^2|^2$, with weights $w = [\sigma_c^2(F_o^2) + (0.01F_o^2)^2]^{-1}$, where $\sigma_c^2(F_o^2)$ is the variance from counting statistics. The neutron scattering amplitudes (fm), 6.02 for Ag, 9.579 for Cl, 5.803 for O, 6.684 for C and -3.7409 for H, were taken from Koester (1977). The Ag scattering amplitude was varied in the final cycles of refinement.

Table 2 gives the refinement conditions and the indices-of-fit at convergence. The parameters of atoms which are symmetry-related in *Cmcm* are found to be strongly correlated (0.95–0.99) when refined independently in space groups *C2cm* and *Cmc2₁*. As a consequence, the positional uncertainties from refinements 2 and 3 are 5–10 times greater than those from refinement 1. Differences in positions obtained in the three space groups at either 18 or 158 K are not significant, the largest being no more than 2σ. Pronounced thermal anisotropy is observed for the Ag atom along the x direction and for one O atom in the yz plane. Relaxing the mirror constraint of *Cmcm* on the silver position by the use of *C2cm* symmetry produces no significant changes in the U^{ij} parameters of the atom. Likewise, in refinements with space group *Cmc2₁*, which allows independent motion of the O atoms related by *Cmcm*, the thermal anisotropy persists. It is therefore concluded that the model is better defined in space group *Cmcm* than in either *C2cm* or *Cmc2₁*. Finally, the Ag^+ disorder model in *Cmcm* suggested by Smith & Rundle (1958) was tested by refinement against the 158 K data; the Ag^+ parameters failed to converge and a static disorder model in *Cmcm* was rejected. The parameters from refinement 1 of Table 2 are reported in Tables 3 and 4.* In the final difference maps based on these refinements, the residual errors $|\Delta\rho|$, as % of ρ at the Cl sites in the F_o syntheses, are $\sim 2.0\%$ for the 158 K data and $\sim 1.0\%$ for the 78 and 18 K data. The average value of the Ag scattering amplitudes from the three refinements, $\bar{b} = 5.88(4)$ fm, is $\sim 4\sigma$ less than

Table 1. *Experimental details*

	18 K	78 K	158 K
Crystal data			
Chemical formula	$AgClO_4.C_6H_6$	$AgClO_4.C_6H_6$	$AgClO_4.C_6H_6$
Chemical formula weight	285.432	285.432	285.432
Cell setting	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Cmcm*	*Cmcm*	*Cmcm*
a (Å)	7.913 (1)	7.973 (1)	8.100 (1)
b (Å)	7.837 (2)	7.857 (1)	7.902 (1)
c (Å)	11.798 (3)	11.777 (2)	11.739 (2)
V (Å^3)	731.6 (5)	737.8 (3)	751.4 (3)
Z	4	4	4
D_x (Mg m^{-3})	2.591 (2)	2.570 (1)	2.523 (1)
Radiation type	Neutron	Neutron	Neutron
Wavelength (Å)	1.046	1.046	1.046
No. of reflections for cell parameters	32	32	32
θ range (°)	22–28	22–28	22–28
μ (mm^{-1})	0.0166	0.0165	0.0162
Temperature (K)	18	78	158
Crystal form	Tablet	Tablet	Tablet
Crystal size (mm)	$2.0 \times 1.7 \times 1.0$	$2.0 \times 1.7 \times 1.0$	$2.0 \times 1.7 \times 1.0$
Crystal color	Colorless	Colorless	Colorless
Data collection*			
Diffractometer	Four-circle diffractometer, beam port H6M, Brookhaven High Flux Beam Reactor	Four-circle diffractometer, beam port H6M, Brookhaven High Flux Beam Reactor	Four-circle diffractometer, beam port H6M, Brookhaven High Flux Beam Reactor
Data collection method	ω–2θ scans	ω–2θ scans	ω–2θ scans
Absorption correction	See text†	See text†	See text†
T_{min}	0.77	0.77	0.77
T_{max}	0.84	0.84	0.84
No. of measured reflections	981	713	838
No. of independent reflections	782	628	800
θ_{max} (°)	53.65	53.65	53.65
Range of h, k, l	$0 \rightarrow h \rightarrow 12$	$0 \rightarrow h \rightarrow 12$	$0 \rightarrow h \rightarrow 12$
	$0 \rightarrow k \rightarrow 12$	$0 \rightarrow k \rightarrow 12$	$0 \rightarrow k \rightarrow 12$
	$0 \rightarrow l \rightarrow 18$	$0 \rightarrow l \rightarrow 18$	$0 \rightarrow l \rightarrow 18$
No. of standard reflections	2	2	2
Frequency of standard reflections (min)	210	210	210
Refinement			
Refinement on	F^2	F^2	F^2
$R(F^2)$‡	0.032	0.032	0.047
$wR(F^2)$§	0.037	0.035	0.045
S¶	1.182	1.084	1.103
Scale factor (k)	1.524 (3)	1.530 (3)	1.536 (3)
No. of reflections used in refinement	782	628	800
No. of parameters used	51	51	51
Weighting scheme	$w = 1/[\sigma_c^2(F_o^2) + (0.01F_o^2)^2]$	$w = 1/[\sigma_c^2(F_o^2) + (0.01F_o^2)^2]$	$w = 1/[\sigma_c^2(F_o^2) + (0.01F_o^2)^2]$
$(\Delta/\sigma)_{max}$	0.15	0.15	0.15
Extinction method	Type I crystal Lorentzian mosaic distribution (Becker & Coppens, 1974)	Type I crystal Lorentzian mosaic distribution (Becker & Coppens, 1974)	Type I crystal Lorentzian mosaic distribution (Becker & Coppens, 1974)
Extinction coefficient	0.046 (2)	0.043 (2)	0.043 (2)
Source of atomic scattering factors	Koester (1977)	Koester (1977)	Koester (1977)

* Measurements at 18 K include scans of systematically extinguished reflections; those at 78 K are limited in high-angle range: $2\theta > 90°$ to approximately 35% of the total number available due to instrument failure.   † Calculated with mass absorption coefficients (μ/ρ) values tabulated (*International Tables for X-ray Crystallography*, 1968, Vol. III, p. 197) for Ag, Cl, O and C and (μ/ρ) of 23.9 cm^2 g^{-1} for chemically bonded H atoms (Koetzle & McMullan, 1980).   ‡ $R(F^2) = \Sigma|F_o^2 - (kF_c)^2|^2/\Sigma F_o^2$.   §$wR(F^2) = [\Sigma w|F_o^2 - (kF_c)^2|^2/\Sigma w(F_o^2)^2]^{1/2}$. ¶$S = [\Sigma w|F_o^2 - (kF_c)^2|^2/(N - P)]^{1/2}$.

that given by Koester (1977), but agrees to within 1σ with the more recent value for b_{Ag}, 5.922 (7) fm, given by Sears (1993). Extinction effects were moderate, with a minimum extinction factor of 0.74 multiplying F_c^2.

The structure analyses were carried out with the crystallographic least-squares refinement program (modified to include the secondary extinction parameters) and the function and error program of Busing, Martin & Levy (1962, 1964); the Fourier summation program of Zalkin (undated); and the thermal ellipsoid plot program of Johnson (1976).

3. Results and discussion

Fig. 1 illustrates the geometry of bonding in the complex at 18, 78 and 158 K, with dimensions derived

Table 2. *Summary of refinements*

Refinement	Number of parameters*	18 K (782 observations)			78 K (628 observations)			158 K (800 observations)		
		$R(F^2)$	$wR(F^2)$	S	$R(F^2)$	$wR(F^2)$	S	$R(F^2)$	$wR(F^2)$	S
1. *Cmcm*	51	0.032	0.037	1.18	0.032	0.035	1.08	0.047	0.045	1.10
2. *C2cm*†	91	0.031	0.035	1.15				0.044	0.042	1.07
3. *Cmc2₁*†	89	0.031	0.036	1.17				0.044	0.042	1.06

* Parameters in each refinement included a scale factor, the unconstrained positional and displacement parameters, the scattering length of Ag and the isotropic extinction parameter (Becker & Coppens, 1974) for a type I crystal with Lorentzian distribution of mosaicity. † The cell origin was defined in refinements by fixing a Cl coordinate (x in *C2cm*; z in *Cmc*$_2$) at its respective value in the *Cmcm* model.

Table 3. *Nuclear positional parameters* $(\times 10^5)$ *for* $AgClO_4.C_6H_6$ *at 18, 78 and 158 K (listed in order of increasing temperature)*

	x	y	z
Ag	0	3950 (12)	25000
	0	3965 (15)	25000
	0	4074 (20)	25000
Cl	0	44631 (8)	25000
	0	44647 (8)	25000
	0	44674 (10)	25000
O(1)	0	33730 (10)	15063 (7)
	0	33803 (12)	15066 (9)
	0	33911 (17)	15061 (13)
O(2)	14834 (9)	55299 (9)	25000
	14720 (11)	55245 (11)	25000
	14489 (13)	55152 (14)	25000
C(1)	17697 (8)	0	0
	17580 (9)	0	0
	17287 (10)	0	0
C(2)	8875 (5)	−11565 (5)	6806 (3)
	8801 (6)	−11553 (6)	6804 (4)
	8677 (7)	−11494 (7)	6804 (4)
H(1)	31434 (17)	0	0
	31196 (20)	0	0
	30750 (23)	0	0
H(2)	15779 (14)	−21081 (13)	11687 (9)
	15612 (16)	−21043 (14)	11686 (10)
	15412 (21)	−20947 (18)	11688 (12)

Table 4. *Nuclear anisotropic displacement parameters* $(\mathring{A}^2 \times 10^4)$ *at 18, 78 and 158 K (listed in order of increasing temperature)*

The displacement factor is: $T = \exp(-2\pi^2 \sum_i \sum_j h_i h_j a_i^* a_j^* U^{ij})$.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag	86 (4)	32 (4)	41 (1)	0	0	0
	226 (5)	78 (6)	78 (1)	0	0	0
	525 (7)	155 (6)	146 (1)	0	0	0
Cl	58 (2)	30 (2)	58 (1)	0	0	0
	103 (2)	61 (3)	101 (1)	0	0	0
	178 (3)	117 (3)	180 (2)	0	0	0
O(1)	106 (3)	96 (3)	115 (3)	0	0	−59 (1)
	181 (4)	205 (5)	250 (4)	0	0	−151 (1)
	349 (7)	383 (7)	458 (6)	0	0	−288 (1)
O(2)	75 (3)	70 (3)	97 (2)	−19 (1)	0	0
	123 (3)	123 (4)	144 (3)	−26 (1)	0	0
	234 (5)	226 (4)	248 (4)	−59 (1)	0	0
C(1)	70 (2)	70 (2)	78 (2)	0	0	4 (1)
	107 (2)	115 (3)	109 (2)	0	0	1 (1)
	179 (3)	208 (3)	177 (3)	0	0	−8 (1)
C (2)	86 (2)	53 (2)	71 (1)	10 (1)	−5 (1)	7 (2)
	140 (2)	88 (2)	92 (2)	16 (2)	−10 (2)	5 (2)
	242 (2)	155 (2)	138 (2)	36 (2)	−20 (2)	5 (2)
H(1)	119 (7)	277 (7)	282 (6)	0	0	36 (1)
	159 (8)	360 (9)	349 (7)	0	0	27 (2)
	227 (13)	532 (11)	486 (10)	0	0	17 (2)
H(2)	230 (4)	185 (4)	234 (4)	59 (4)	−28 (4)	66 (16)
	316 (5)	233 (6)	266 (5)	73 (5)	−38 (4)	68 (16)
	480 (7)	341 (6)	350 (7)	132 (7)	−66 (5)	74 (17)

from the nuclear positions given in Table 3. The dimensions at 18 K are quoted in the following discussion unless otherwise stated. The coordination of Ag^+ is shown in Fig. 2 with probability ellipsoids representing the atomic displacements from nuclear mean positions at 18, 78 and 158 K. Fig. 3 depicts the crystal structure and atomic displacements in the lattice at 158 K. For each atom the magnitudes of the mean-square displacements (m.s.d.'s), $\langle u_i^2 \rangle$, $i = 1, 2, 3$, along principal axes of the probability ellipsoids were plotted against temperature. The components $\langle u_1^2 \rangle$ and $\langle u_2^2 \rangle$ of O(1) and $\langle u_1^2 \rangle$ of Ag^+ show strong temperature dependencies, which between 78 and 158 K are ~ 2.5–3.0 times greater than those for the corresponding m.s.d.'s of the other heavy atoms. Residual m.s.d.'s at 0 K estimated by three-point extrapolation are comparable within the range $7.5 \pm 2.5 \times 10^{-4}\ \mathring{A}^2$, except for those of H atoms, which are larger by factors of two. The residual m.s.d.'s of hydrogen may be attributed mainly to zero-point motion; whereas residuals of the heavy atoms suggest static disorder at levels which are not resolved by the diffraction data.

3.1. Geometry of the complex

The general features of the $AgClO_4.C_6H_6$ complex were correctly described by Smith & Rundle (1958). At the low temperatures of our study the structure is ordered in space group *Cmcm* (see above). The Ag^+ ion is in a single-minimum potential well which is centered over a C—C bond and slightly outside the C_6 ring. Our analysis reveals an unusually low barrier for motion of Ag^+ parallel to the nearest C—C bond; the disordered model for the room-temperature structure that was favored by Smith and Rundle reflects pronounced thermal anisotropy of Ag^+ in this direction. Distortions of the benzene molecule from D_{6h} symmetry are small, as Gilson & McDowell (1964) anticipated, but significant in terms of the precision of the present analysis.

The benzene molecules occupy sites of $2/m$ symmetry with the C_6 rings being planar to within experimental error. With respect to bond distances and in-plane angles, the molecule is slightly distorted from D_{6h} symmetry (see Fig. 1). The four C—C distances of the type C(1)—C(2) are 1.398 (1) Å. This value is essentially the same as that found in deuterobenzene at 15 K, 1.3972 (5) Å (Jeffrey, Ruble, McMullan & Pople, 1987), and that found in the gas phase by electron diffraction, 1.397 (3) Å (Almenningen, Bastiansen & Fernholt, 1953), and by analysis of the rotational fine structure in the Raman spectrum, 1.397 (1) Å (Langseth & Stoicheff, 1956). The two distances of the type C(2)—C(2) are significantly lengthened by silver complexation to 1.405 (1) Å. The C—H bonds are equal in length within experimental error, 1.088 (1) Å. This mean value is indistinguishable from values measured in the gas phase [1.083 (5) (Almenningen, Bastiansen & Fernholt, 1953), 1.084 (6) Å (Langseth & Stoicheff, 1956)].

In addition to very slightly lengthening the complexed C—C bonds, the principal effect of Ag^+ on the benzene molecule is to push the two nearest H atoms 0.064 (1) Å away from the C_6 plane. This distortion corresponds to a C(1)C(2)C(2)—H(2)C(2)C(2) dihedral angle of 3.9 (1)°. The out-of-plane displacement of hydrogen in a direction *away from* silver is of the same order of magnitude as a comparable bending *toward* the metals in benzene chromium tricarbonyl, 0.03 Å (Rees & Coppens, 1973), and in several cyclopentadienyl complexes (Takusagawa & Koetzle, 1979, and references therein). Typical of the latter displacements are 0.030 (7) Å in solid ferrocene, 0.07 (2) Å in gaseous ferrocene, 0.06 (2) Å in gaseous biscyclopentadienyl chromium and 0.027 (5) Å in solid ferrocene dicarboxylic acid. As is the case here, the olefinic hydrogens in Zeise's salt $KPtCl_3(C_2H_4).H_2O$ (Love, Koetzle, Williams, Andrews & Bau, 1975) are displaced away from the metal, but to a greater extent, 0.156 (1) and 0.171 (1) Å. The direction and greater magnitude of distortion of ethylene upon coordination is consistent with reorganization of electrons about carbon toward a tetrahedral configuration. Distortion in the aromatic complexes cited has been described in terms of a reorientation of a primarily p-π, p-σ (or p-π, $sp^2 - \sigma$) carbon electron configuration, so as to allow the p-π orbitals to point inward toward the metal (Haaland, 1975). The form of distortion in the silver complex is compatible with either type of electron
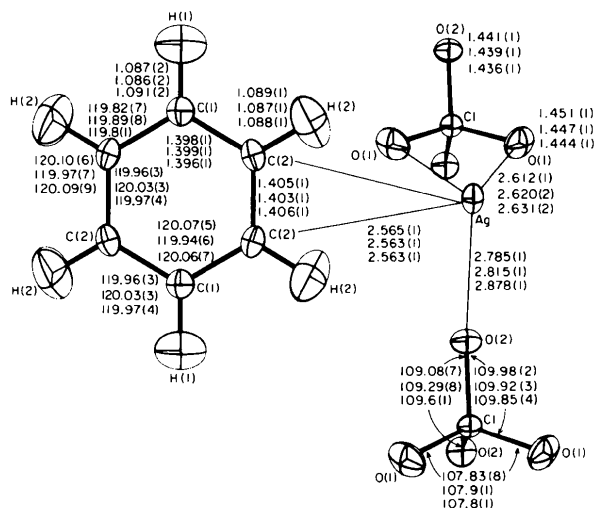

Fig. 1. Atomic notation, displacement ellipsoids (95% probability surfaces at 18 K) and dimensions at 18 (upper value), 78 and 158 K (lower value). The figure is a composite of two diagrams; *cf.* Fig. 2 for true perspective.
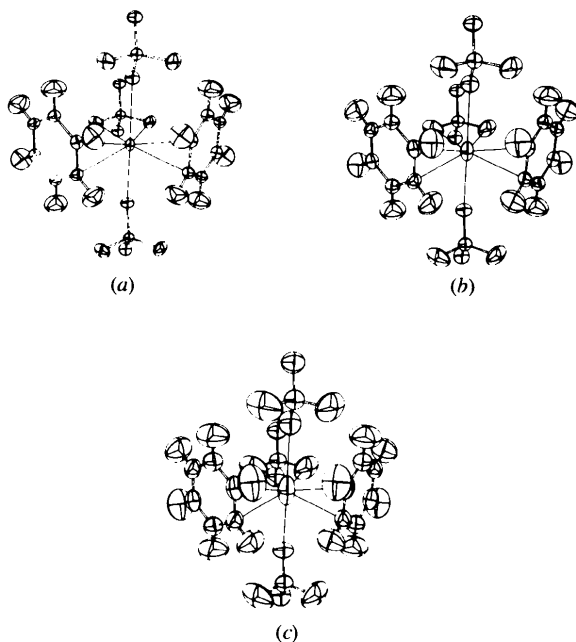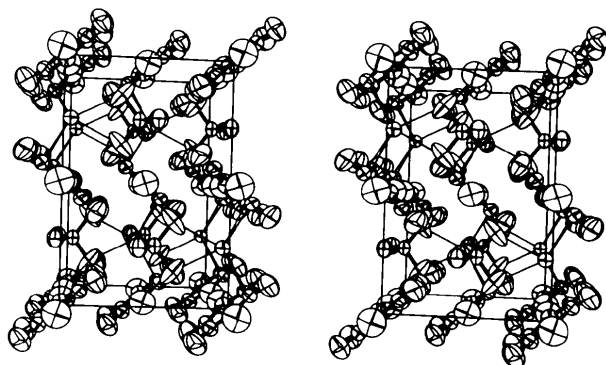

Fig. 2. Coordination around Ag^+ at (a) 18, (b) 78 and (c) 158 K. Displacement ellipsoids enclose 95% probability distributions.

Fig. 3. Stereoscopic diagram of the $AgClO_4.C_6H_6$ structure at 158 K viewed along a with b horizontal and c vertical. Displacement ellipsoids at 95% probability.

reconfiguration at carbon, since the Ag$^+$ lies outside the C$_6$ ring, but in view of the weakness of bonding in these complexes the latter description (slightly rotated σ, π) seems more appropriate.

3.2. The crystal structure

Benzene.Ag$^+$ π bonding in the crystal occurs along c in infinite chains, $\cdots$/Ag\Ag/Ag\$\cdots$, where / and \ represent the benzene molecules as viewed along a in Fig. 3. The shortest interaction distances between ions and molecules are observed in the units of structure repeating along **b** shown in Fig. 4. The bond distance Ag to C(2)—C(2), bond-center (C$_c$), and the angle C$_c$—Ag—C$_c$ are, respectively, 2.467(1), 2.466(1), 2.465(1) Å and 120.9(1), 120.7(1), 121.1(1)° at 18, 78 and 158 K. The interplanar angles between benzene molecules linked by Ag$^+$ ions decrease slightly with increasing temperature from 83.1(1) (18 K) to 82.7(1)° (158 K). This accordion-like folding is responsible for the anomalous contraction of the c lattice parameter with increasing temperature. The Ag$^+$ ions are displaced 0.66 Å along **b** from sites between two C$_c$ bond centers, giving angles of 102.0° (18 K) between the C$_6$ and C(2)—C(2)—Ag planes. Similar geometric features in Ag$^+$ π complexes are common (McKechnie & Paul, 1968), the largest dihedral value of 115° being found in norbornadiene.2AgNO$_3$ (Baenziger, Haight, Alexander & Doyle, 1966; Marsh & Herbstein, 1983). O(2) atoms lie near lines where extensions of C$_6$ planes intersect and approach H(2) atoms at distances, 2.429(1), 2.436(1) and 2.452(1) Å (18, 78 and 158 K), which are less than the sum of van der Waals radii, 1.4 Å for oxygen and 1.2 Å for hydrogen (Pauling, 1960). O(2) and H(2) atoms at 18 K are displaced 0.137(1) and 0.062(1) Å from the C$_6$ planes on sides opposite the Ag$^+$ ions; thus, their van der Waals interactions would *oppose* the observed out-of-plane deformation of benzene attributed above to the influence of Ag$^+$ on the π cloud. O(1) atoms are in mean positions lying at distances 3.110(1), 3.113(1) and 3.119(1) Å (18, 78 and 158 K) from the C(2)—C(2) bond centers (C$_c$). The O(1)$\cdots$C(2) distances are 3.189(1), 3.191(1) and 3.197(1) Å. These oxygen$\cdots$benzene separations are within the expected range of contact, 3.1–3.2 Å, for an oxygen approach normal to the benzene plane and show greater invariance with temperature than other van der Waals separations in the structure. The resulting short-range repulsive interactions probably constrain the large amplitude atomic displacements observed for O(1) to directions nearly tangential to the benzene rings (see Figs. 2 and 3).

Stacking along a of ClO$_4^-$ and C$_6$H$_6$ molecules, with O(1)$\cdots$H(1) contacts of 2.635(1), 2.649(1) and 2.678(1) Å at 18, 78 and 158 K, limits the minimum O(2)$\cdots$Ag$^+$ approach distances to 2.785(1) Å, which

are ~ 0.2 Å longer than those found in several other silver perchlorate-aromatic complexes (Rodesiler, Griffith & Amma, 1972). Thermal motion of Ag$^+$ along **a**, parallel to the C(2)—C(2) bonds, is therefore constrained principally by π bonding between silver and benzene molecules. The pronounced temperature dependence of the displacement amplitude of Ag$^+$ along the C(2)—C(2) bonds, Fig. 2 and Table 4, indicates a shallow potential well in this direction.

With increasing temperature, the mean ionic and van der Waals separation distances cited above increase significantly. In ClO$_4^-$ the mean distances between covalently bonded atoms (Fig. 1) are foreshortened by 0.005 (3.5 e.s.d.'s) and 0.007 Å (5.0 e.s.d.'s), for O(2) and O(1), respectively, from 18 to 158 K. By contrast, in C$_6$H$_6$ the bond lengths show no systematic trend between 18 and 158 K, nor do they differ significantly within their pooled e.s.d.'s (0.002 Å). The benzene.Ag$^+$ π interaction distance falls into this latter class.

3.3. Temperature dependence of atomic displacements

Further analysis of the U^{ij} parameters (Table 4) was carried out to obtain a deeper insight into the effects of temperature on the structure. Correlated atomic displacements between pairs or among sets of atoms within the ClO$_4^-$ and C$_6$H$_6$ groups were examined and tested under the assumption of rigid-body motion (Schomaker & Trueblood, 1968). For a rigid group, the mean-square displacements $\langle u^2 \rangle$ of any two atoms in directions toward each other must be equal. A corollary
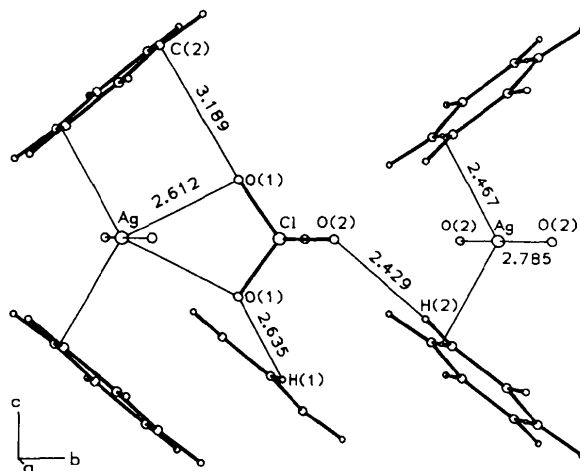

Fig. 4. Perspective view of packing arrangement along b showing shortest distances (Å) between Ag$^+$, ClO$_4^-$ and C$_6$H$_6$ at 18 K. Atoms Ag and Cl lie on the line of intersecting mirrors at ($x = 0, z = \frac{1}{4}$) of *Cmcm*. Centers of the four C$_6$H$_6$ molecules fully outlined are at (0,0,0; 0,1,0; 0,0,$\frac{1}{2}$; 0,1,$\frac{1}{2}$) and that of the incomplete molecule is at ($-\frac{1}{2},\frac{1}{2},\frac{1}{2}$). O(2) atoms above and below Ag atoms at (0, y, $\frac{1}{4}$; 0, 1 + y, $\frac{1}{4}$) are related to the O(2) position of Table 3 by ($-\frac{1}{2}+x, -\frac{1}{2}+y, z; \frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$) and ($-\frac{1}{2}+x, \frac{1}{2}+y, z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$), respectively.

Table 5. *Differences,* $\Delta_{A,B}$ *($\dot{A}^2 \times 10^4$), in mean-square-displacement amplitudes along vectors between atom-pairs A,B of the perchlorate ion and of the benzene molecule, derived from the U^{ij} parameters in Table 4. The triads give values at 18, 78 and 158 K*

Cl—O(1)*	Cl—O(2)*	O(1)—O(2)	O(1)—O(1)†	O(2)—O(2)†
6	4	−23	0	0
9	4	−79	0	0
1	18	−156	0	0

C(1)—C(2)*	C(1)—C(2)	C(2)—C(2)*†	C(2)—C(2)†
−2	2	0	0
2	5	0	0
−2	5	0	0

H(1)—C(1)*	H(1)—C(2)	H(1)—C(2)	H(2)—C(2)	H(2)—C(1)	H(2)—C(2)	H(2)—C(1)	H(2)—C(2)*
49	63	80	75	60	65	72	56
52	74	81	82	60	66	72	62
48	68	90	73	58	73	63	67

* Bond direction.   † Zero by virtue of symmetry.

Table 6. *Bond lengths (Å) with thermal-motion corrections. The triads give values at 18, 78 and 158 K*

Benzene	Uncorrected	Corrected*†	Perchlorate	Uncorrected	Corrected†	Corrected‡
C(1)—C(2)	1.398	1.399	Cl—O(1)	1.451	1.455	1.456
	1.399	1.400		1.447	1.457	1.460
	1.396	1.400		1.444	1.462	1.469
C(2)—C(2)	1.405	1.406	Cl—O(2)	1.441	1.445	1.444
	1.403	1.406		1.439	1.446	1.443
	1.406	1.411		1.436	1.449	1.444
C(1)—H(1)	1.087	1.088				
	1.086	1.088				
	1.091	1.094				
C(2)—H(2)	1.089	1.090				
	1.087	1.088				
	1.088	1.091				

* Internal vibrations removed in benzene (Johnson, 1970).   † Rigid-body correction.   ‡ Riding correction.

Table 7. *Harmonic model of silver motion*

Assuming an average mass of 107.87 a.m.u. The e.s.d.'s do not include uncertainty in temperature; an error of 2° changes $\bar{v}$ by 1.5σ or less.

Temperature (K)	$\bar{v}(U^{11})$ (cm^{-1})	$\bar{v}(U^{22})$ (cm^{-1})	$\bar{v}(U^{33})$ (cm^{-1})
18	24.3 (7)	51 (6)	41 (4)
78	27.7 (4)	48 (2)	48 (2)
158	25.6 (3)	47 (1)	49 (1)

is that the difference, if meaningful, must represent relative internal motion. Table 5 examines the differences, $\Delta_{A,B} = \langle u^2 \rangle_A - \langle u^2 \rangle_B$, between atom pairs in the ClO_4^- and C_6H_6 groups. For the ClO_4^- ion the differences are consistent with 'rigid bonds' (Hirshfeld, 1976) within 2 e.s.d.'s at 18 and 78 K, but they indicate unexpected 'softness' along two edges of the tetrahedron. These increasingly larger $\Delta_{O,O}$ values may be attributed to temperature-dependent static disorder or to an apparent oxygen O(1) scissoring motion in response to Ag^+ displacements at the comparatively short $Ag^+\cdots O(1)$ interaction distance (see Figs. 1 and 2). For the C_6H_6 molecule the

displacement differences are consistent with rigidity in the carbon ring and are indicative of significant intramolecular vibrational modes for the H atoms. The pattern of $\Delta_{H,C}$ values appears to be temperature-independent between 18 and 158 K: the dispersions from the mean $\Delta_{H,C}$ values in each listed H—C direction give an overall e.s.d. of 4×10^{-4} Å^2, which is no greater than the e.s.d.'s derived from the U^{ij} parameters. Motions due to high-frequency internal vibrational modes would be expected to be essentially independent of temperature in this range (Willis, 1969). In the H—C bond direction the excess hydrogen motion at the three temperatures [49 (4), 52 (6), 48 (7) $\times 10^{-4}$ Å^2 in C(1)—H(1); 56 (4), 62 (4), 67 (7) $\times 10^{-4}$ Å^2 in C(2)—H(2)] agree reasonably well with the excess of 46×10^{-4} Å^2 calculated by Johnson (1970) from benzene spectra.

For both ClO_4^- and C_6H_6 provisional corrections for librational motion were applied to bond lengths based on the rigid-body models, notwithstanding the serious internal deformations apparent in ClO_4^- (Table 5) and the lack of statistically significant differences among corresponding uncorrected bond lengths in C_6H_6.

Contributions from internal C—H motion calculated by Johnson (1970) were subtracted* from the observed U^{ij} components of hydrogen and carbon. As Table 6 shows, the use of the rigid-body model for this structure produces no significant changes in the benzene bond lengths at 18 and 78 K, but produces an apparent over-correction at 158 K, with an overall deterioration in agreement among corresponding bond lengths that is marginally significant. For the perchlorate ion the librational correction is clearly excessive and approximately twice the value needed to achieve a temperature-independent result. The apparent center of libration is displaced from Cl in a direction away from the Ag$^+$ ion, as revealed by an examination of the displacement ellipsoids (Fig. 3). Alternatively, it is reasonable to apply the Busing & Levy (1964) riding model to the motion of oxygen in a perchlorate ion. This model results in an overcorrection for the Cl—O(1) bond length; however, it works exceptionally well for Cl—O(2), leading to an essentially temperature-independent bond length value.

Attempts were made to fit the displacements of Ag$^+$ to both Debye and single-frequency (Einstein) thermal models (Cruickshank, 1956). The Debye model failed, despite introducing a variable effective mass. A single-frequency potential of the type $\langle u \rangle^2 = (h/8\pi^2 mcv)\coth(hcv/2kT)$ (Cruickshank, 1956; James, 1965) was satisfactory, yielding the $\bar{v}$ values listed in Table 7. The values of each $\bar{v}$ agree with their mean within e.s.d.'s. This agreement with the prediction of a single-frequency model is perhaps fortuitous. However, it is worth noting that anharmonic potentials which are based on the same fundamental concept of the one-particle potential have been used with success in analyzing simpler solids (Dawson, Hurley & Maslen, 1967; Mair & Wilkins, 1976; Dawson, 1970; Moss, McMullan & Koetzle, 1980).

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* Calculations were performed with a computer program (Craven, 1982) that transformed the vibrational directions and amplitudes between the molecular coordinate system and crystallographic U^{ij} components.

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