

The effect of counter ions on the symmetry of $\text{Cu}(\text{NO}_2)_6^{4-}$ is puzzling. We have shown that K_2Ba^{4+} and K_2Ca^{4+} give an *elongated* tetragonal environment around Cu^{II} at 295°K. However, preliminary results indicate that K_2Pb^{4+} and $\text{Rb}_2\text{Pb}^{4+}$ give a *compressed* tetragonal distortion below 280 and at 295 K, respectively.

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1,2-Diphenylethanesilver(I) Perchlorate

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Abstract. $[(\text{C}_6\text{H}_5)_2(\text{CH}_2)_2]\text{Ag}^+\text{ClO}_4^-$, orthorhombic, *Pbnm*, $Z=4$, M.W. 389.5, $a=5.871$ (1), $b=12.575$ (2), $c=18.731$ (3) Å, $D_x=1.87$, $D_m=1.7-2.1$ g cm⁻³ (by flotation), $\lambda(\text{Mo } K\alpha)=0.71068$ Å, $\mu(\text{Mo } K\alpha)=16.2$ cm⁻¹, $R(\text{final})=0.076$. The Ag atom is disordered in such a way that some Ag's have square-pyramidal and others have square-planar coordination geometry from bonding to oxygen of perchlorate and π -bonding to benzene.

Introduction. As part of a program examining the interaction between Ag^I and aromatic hydrocarbons (Griffith & Amma, 1971), we synthesized the title compound by reacting anhydrous AgClO_4 and 1,2-diphenylethane (DPE) in toluene. Diffraction quality crystals were grown by slow evaporation of the solution and sealed in thin-walled glass capillaries for X-ray studies. Weissenberg and precession photographs $hk0 \cdot \cdot hk7$, $h0l$, $0kl$ revealed orthorhombic symmetry and the extinctions $0kl$, $k=2n+1$ and $h0l$, $h+l=2n+1$, establishing the possible space group as *Pbnm* or *Pbn2₁*. The correct choice of space group was *Pbnm* as shown by the structure analysis. A least-squares treatment of χ , φ , ω and 2θ values of 20 well centered

reflections gave the cell dimensions: $a=5.871$; $b=12.575$ (2); $c=18.731$ (3) Å; $\lambda=0.71068$ Å. The density was only bracketed between the values 1.70 and 2.10 g cm⁻³ since the crystals disintegrated in solvents of appropriate density. Assuming four molecules per cell the calculated density is 1.87 g cm⁻³. A crystal with dimensions 0.20 × 0.20 × 1.0 mm was mounted such that the long direction (*c*) was approximately parallel to the φ axis. Reflections were measured by a θ - 2θ scan technique with Zr-filtered Mo $K\alpha$ radiation and a scan time of 81 s at a rate of 0.0333° s⁻¹, and the backgrounds were counted at $\pm 1.35^\circ$ 2θ of peak maximum for 20 s. The counting rate never exceeded 5000 c s⁻¹. After every ten reflections a standard peak was measured to monitor stability of electronics, crystal decomposition and alignment. (A peak of average intensity approximately in the center of the χ , φ , 2θ range was chosen for maximum sensitivity.) The variation of the standard peak was σ or less throughout the data collection where $\sigma(I)=[I_{\text{scan}}+(2.025)^2(B_1+B_2)]^{1/2}$. Reflections were considered absent if the integrated intensity was less than $2[(2.025)^2(B_1+B_2)]^{1/2}$, (2σ of background). From the approximately 1400 reflections measured, 447 were considered non-zero by the above criterion. (The disorder found for the Ag atoms is, no doubt, the reason for the abbrevi-

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ated observed data set.) With Mo $K\alpha$ radiation the linear absorption coefficient (μ) was found to be 16.2 cm^{-1} . No absorption corrections were made. Early in the structure analysis the disorder mentioned above and below was found. Such a disorder inherently places severe limitations on the intensity data (a systematic source of error that is not really correctable) and imposes practical limits on the refinement. With this in mind we decided against making any absorption corrections.

The structure was solved by standard heavy-atom methods and refined by full-matrix least-squares calculations with anisotropic temperature factors for Ag, Cl, O. Anomalous dispersion corrections were made for Ag and Cl. The only non-routine aspect of the structure solution and refinement was the discovery that the Ag atom was disordered between two positions with non-equal occupancy. With all other variables held constant at the isotropic level the site occupancies were determined to be 0.7 and 0.3 for Ag and Ag*, respectively. Since the temperature factors and the site occupancy numbers are correlated, these site occupancy numbers were held fixed for the remainder of the refinement. There is no evidence for disorder in other parts of the structure. The similar behaviors of the disordered atoms upon further refinement gives credence to this procedure. The function minimized was $\sum(F_o - F_c)^2$. The scattering factors for Ag^I, Cl⁻ and neutral oxygen and carbon were from Cromer & Waber (1965). The effects of anomalous dispersion were included in the structure-factor calculations by addition to F_c (Ibers & Hamilton, 1964), the values of

$\Delta f'$ and $\Delta f''$ for Ag^I were those given by Cromer (1965).

The refinement included anisotropic temperature factors for Ag, Cl and O atoms. For those atoms lying in the crystal crystallographic mirror one of the principal axes of the thermal ellipsoid must be normal to this mirror; therefore, for these atoms β_{23} , β_{12} , and $\beta_{13} = 0$, and were not varied. The refinement converged to a final R of 0.076. The shifts of parameters for the last cycle of refinement were 0.2 standard deviation or less. There is no evidence for the lower-symmetry space group ($Pbn2_1$), i.e. large thermal displacements from the mirror or unusual thermal motions of molecules not in the mirror.

Final atomic positional and thermal parameters are in Table 1. Interatomic distances and angles, dihedral angles between normals to planes and their errors were computed using parameters and variance-covariance matrix from the last cycle of full-matrix least-squares refinement, and are given in Fig. 1.*

Computer programs used in this structure determination were *ORFLS* (Busing, Martin & Levy, 1962) with local modifications, *ERFR-3* (Harris, 1963), *ORFFE* (Busing, Martin & Levy, 1964) with local modifications, and *ORTEP* (Johnson, 1965). Least-

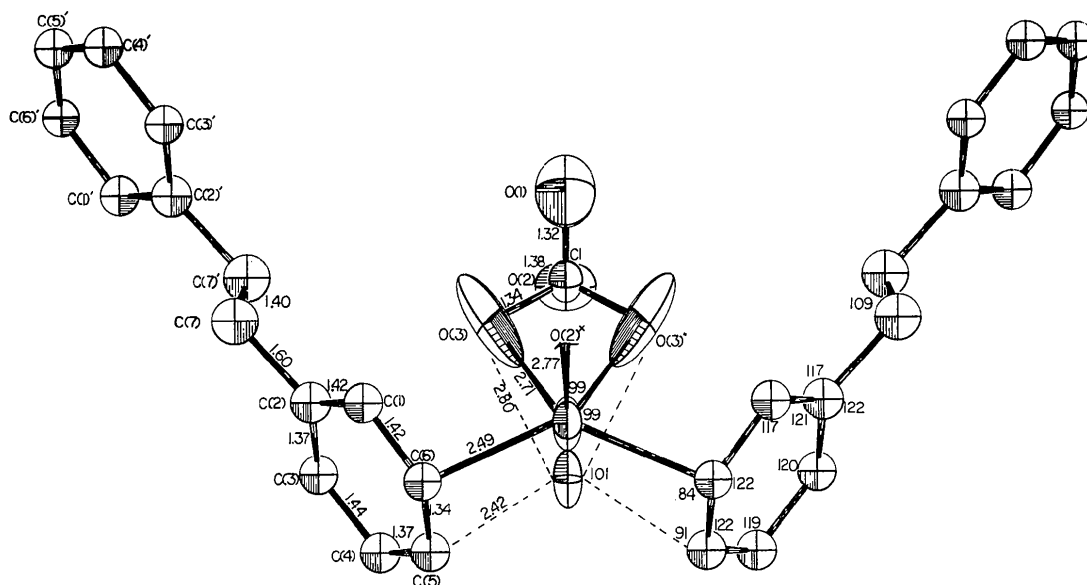


Table 1. *Final atomic positional and thermal parameters*

Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. (—) indicates a fixed parameter.

	<i>x</i>	<i>y</i>	<i>z</i>
Ag	0.3105 (9)	0.3565 (5)	0.2500 (—)
Ag*	0.440 (2)	0.294 (1)	0.2500 (—)
Cl	0.740 (2)	0.5180 (8)	0.2500 (—)
O(1)	0.683 (6)	0.619 (3)	0.2500 (—)
O(2)	0.975 (5)	0.511 (2)	0.2500 (—)
O(3)	0.652 (5)	0.473 (3)	0.192 (1)
C(1)	0.163 (4)	0.381 (2)	0.093 (1)
C(2)	0.368 (4)	0.382 (2)	0.053 (1)
C(3)	0.522 (4)	0.301 (2)	0.059 (1)
C(4)	0.476 (4)	0.212 (2)	0.106 (1)
C(5)	0.278 (4)	0.213 (2)	0.144 (1)
C(6)	0.127 (4)	0.292 (2)	0.139 (1)
C(7)	0.394 (4)	0.476 (2)	—0.005 (1)

Anisotropic temperature factors of the form:

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^3$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag	58 (3)	13.1 (7)	1.7 (1)	—8 (1)	0 (—)	0 (—)
Ag*	55 (6)	15 (2)	1.6 (3)	—1 (2)	0 (—)	0 (—)
Cl	31 (4)	8 (1)	2.3 (2)	—1 (2)	0 (—)	0 (—)
O(1)	82 (20)	24 (5)	8 (2)	29 (9)	0 (—)	0 (—)
O(2)	34 (12)	11 (3)	8 (2)	—1 (4)	0 (—)	0 (—)
O(3)	100 (16)	40 (5)	9 (1)	—4 (7)	—15 (4)	—15 (2)

Isotropic temperature factors for carbon

	<i>B</i>	<i>B</i>	<i>B</i>	<i>B</i>			
C(1)	4 (1)	C(3)	4 (1)	C(5)	4 (1)	C(7)	6 (2)
C(2)	5 (1)	C(4)	4 (1)	C(6)	4 (1)		

squares programs for lattice parameters and diffractometer angles are local programs.

Discussion. The crystal structure is composed of pleated —DPE—Ag—DPE—Ag— ribbons weakly held together by perchlorate ions which alternate with the Ag⁺ ions along the pleats to form AgClO₄ chains (see Figs. 1 and 2). A glance at the local environment of the silver atoms reveals two Ag—aromatic interactions per Ag atom. The Ag⁺ atoms as specified by the appropriate dihedral angles are clearly π -bonded to the aromatic moieties. Many of the packing and bonding features are what we have come to expect for this type of compound (Griffith & Amma, 1971). The Ag—O interactions that determine the completion of the coordination sphere about Ag are all long (2.71–2.80 Å). Since these interactions are weak, it is expected that there be little

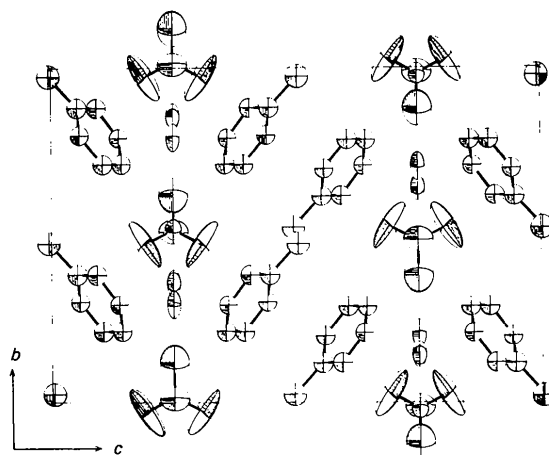


Fig. 2. An ORTEP (Johnson, 1965) perspective view of the 1,2-diphenylethane.AgClO₄ structure down the *a* axis. The AgClO₄ chains propagate normal to the plane of the paper.

difference energetically between square-planar and square-pyramidal geometry for Ag⁺ in the present structure. Hence, it is not surprising (after the fact) that the Ag atoms are disordered.

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