

The crystal structure of silver(I) 2,4,5-trichlorophenolate

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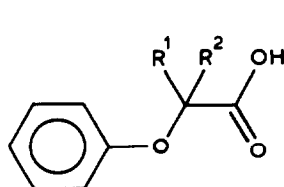
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Abstract

The crystal structure of silver(I) 2,4,5-trichlorophenolate has been determined by X-ray diffraction and refined to a residual $R = 0.031$ for 1072 observed reflections. Crystals are orthorhombic, space group $Pccn$ with 8 molecules in a cell of dimensions, a 11.455(4), b 23.75(1), c 5.645(1) Å. Each silver in the polymeric structure is bonded to three independent phenolate oxygens (Ag–O range, 2.317–2.543(3) Å; O–Ag–O range, 86.5–106.5(2)°). In addition there is an unusual symmetrical and directed phenyl carbon–silver bond (Ag–C, 2.443(5) Å) that completes a trigonal pyramidal stereochemistry about silver.

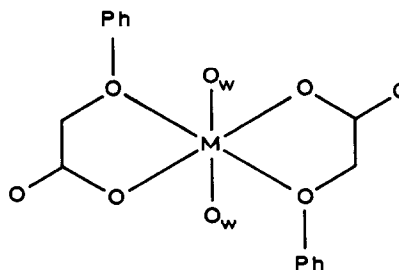
Introduction

An investigation of the structural systematics of metal complexes of the phenoxyalkanoic acids (1) reveals only occasional examples in which there is the bidentate chelate mode (2) [1–6]. Subsequently, a survey of the Cambridge Crystallographic



(1)

($R^1, R^2 = \text{Me}, \text{H}$)



(2)

Data File revealed no examples of this type involving silver(I) or of complexes with a Ag–O–phenyl bond system. It was therefore decided to attempt the preparation and characterization of some silver(I) phenolates. Reported here is the preparation and crystal structure determination of the anhydrous complex silver(I) 2,4,5-trichlorophenolate.

Experimental

Preparation

The complex was prepared by adding to a hot ammoniacal solution of silver nitrate in 50% ethanol/water, an equimolar amount of 2,4,5-trichlorophenol in ethanol. After several weeks standing at room temperature in the dark, a small quantity of pale brown needles grew from a dark non-crystalline solid matrix of unknown identity. Elemental analysis and infrared spectra indicated an anhydrous compound (Found: C, 23.8; H, 0.68%. $C_6H_2AgCl_3O$ calcd.: C, 23.7; H, 0.66%), and this was confirmed by single crystal preliminary data and a density measurement.

Crystal data. $C_6H_2AgCl_3O$, $M = 362.3$; orthorhombic, space group $Pccn$ * (C_{2h}^{10} , No. 56), a 11.455(4), b 23.75(1), c 5.645(1) Å, V 1535.8(8) Å³, $d_{\text{expt}} = 2.61$ (flotation in $CHCl_3/CHBr_3$), d_{calcd} ($Z = 8$) 2.631 g cm⁻³, $F(000) = 1152$, $\mu(\text{Mo-K}\alpha)$ 35.1 cm⁻¹.

Data collection

X-Ray diffraction data were collected at 293 K from a crystal of dimensions $0.28 \times 0.20 \times 0.10$ mm on a Nicolet R3m four-circle diffractometer, using monochromatic Mo- $K\alpha$ X-radiation (λ 0.71069 Å). During the collection a decay of less than 1% in the intensities of two standards indicated no significant crystal decom-

Table 1

Atomic coordinates ($\times 10^4$ except H, $\times 10^3$) and equivalent isotropic thermal parameters (Å², $\times 10^3$). U_{eq} * is defined as $(U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} */ U_{iso}
Ag	1576.1(4)	1935.3(2)	1172.3(8)	37.9(3)*
C(1)	738(4)	1674(2)	-3562(9)	30(3)*
C(2)	680(4)	1095(2)	-4035(9)	32(3)*
Cl(2)	1536(1)	824(1)	-6291(3)	46.3(8)*
C(3)	-39(4)	736(2)	-2757(11)	38(3)*
C(4)	-723(5)	939(2)	-941(10)	37(3)*
Cl(4)	-1573(1)	472(1)	664(3)	57.5(9)*
C(5)	-716(4)	1505(2)	-451(10)	33(3)*
Cl(5)	-1597(1)	1783(1)	1746(3)	52.1(9)*
C(6)	-1(4)	1870(2)	-1727(9)	29(3)*
O(7)	1424(3)	2019(1)	-4749(7)	31(2)*
H(3)	0(3)	35(2)	-342(8)	55(17)
H(6)	-11(3)	232(2)	-155(7)	32(17)

* Symmetry operations: $\pm[(x, y, z), (a); (x, \frac{1}{2} - y, \frac{1}{2} + z), (b); (\frac{1}{2} - x, y, \frac{1}{2} + z), (c); (\frac{1}{2} - x, \frac{1}{2} - y, z), (d)]$.

Table 2

Bond distances (Å) and angles (degrees)

<i>a. distances</i>			
Ag–O(7) ^b	2.543(3)	C(2)–C(3)	1.388(8)
Ag–O(7) ^c	2.358(3)	C(2)–Cl(2)	1.731(6)
Ag–O(7) ^{e a}	2.317(3)	C(3)–C(4)	1.376(8)
Ag–C(6) ^a	2.443(5)	C(4)–C(5)	1.375(7)
C(1)–C(2)	1.402(7)	C(4)–Cl(4)	1.730(6)
C(1)–C(6)	1.416(7)	C(5)–C(6)	1.393(7)
C(1)–O(7)	1.318(6)	C(5)–Cl(5)	1.730(6)
<i>b. angles</i>			
O(7) ^b –Ag–O(7) ^c	86.5(2)	O(7)–C(1)–C(2)	122.7(4)
O(7) ^b –Ag–O(7) ^e	96.5(2)	O(7)–C(1)–C(6)	121.6(4)
O(7) ^b –Ag–C(6) ^a	82.8(2)	C(2)–C(1)–C(6)	115.7(5)
O(7) ^c –Ag–O(7) ^e	106.5(2)	C(1)–C(2)–C(3)	122.1(5)
O(7) ^c –Ag–C(6) ^a	125.1(2)	C(1)–C(2)–Cl(2)	118.5(4)
O(7) ^e –Ag–C(6) ^a	128.0(2)	C(3)–C(2)–Cl(2)	119.3(4)
Ag–O(7) ^c –C(1) ^e	119.8(2)	C(2)–C(3)–C(4)	120.8(5)
Ag–O(7) ^b –C(1) ^b	123.0(2)	C(3)–C(4)–C(5)	119.2(5)
Ag–O(7) ^c –C(1) ^c	114.5(2)	C(3)–C(4)–Cl(4)	119.2(4)
Ag–C(6) ^a –C(1) ^a	93.9(2)	C(5)–C(4)–Cl(4)	121.6(4)
Ag–C(6) ^a –C(5) ^a	97.3(2)	C(4)–C(5)–C(6)	120.6(5)
		C(4)–C(5)–Cl(5)	121.0(4)
		C(6)–C(5)–Cl(5)	118.4(4)
		C(5)–Cl(6)–C(1)	121.7(5)

^a $e = x, y, 1 + z$.

position despite progressive greying of the crystal. Of 1336 unique reflections collected up to $2\theta\ 52^\circ$, 1072 with $I > 2.5\sigma(I)$ were considered observed and were used in structure analysis. Data were processed using a learnt profile fitting procedure [7] and were corrected for Lorentz and polarization effects and for absorption.

Structure solution and refinement

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares to residuals $R [= \Sigma \|F_o| - |F_c| \| / \Sigma |F_o|] = 0.031$ and $R_w [= \Sigma w \|F_o| - |F_c| \|^2 / \Sigma w |F_o|^2]^{1/2} = 0.032$. A value of $w = 1.6 / (\sigma^2 F_o + 2.7 \times 10^{-4} F_o^2)$ was used. Hydrogens were located by difference methods and their positional and thermal parameters refined. SHELX-76 [8] was used for all computations while neutral atom scattering factors and f' , f'' terms for anomalous dispersion were taken from ref. 9. Final atomic parameters are given in Table 1 and bond distances and angles in Table 2. Lists of anisotropic thermal parameters and observed and calculated structure factors are available from the authors.

Discussion

The coordination about silver in the title compound comprises an approximate pyramidal array of oxygens from three different phenolate groups (Fig. 1) Ag–O(7)^b ($x, \frac{1}{2} - y, \frac{1}{2} + z$) (2.543(3) Å); Ag–O(7)^c ($\frac{1}{2} - x, y, \frac{1}{2} + z$) (2.358(3) Å) and Ag–O(7)^e ($x, y, 1 + z$) (2.317(3) Å). The O–Ag–O angles range from $86.5(2)^\circ$ to $106.5(2)^\circ$.

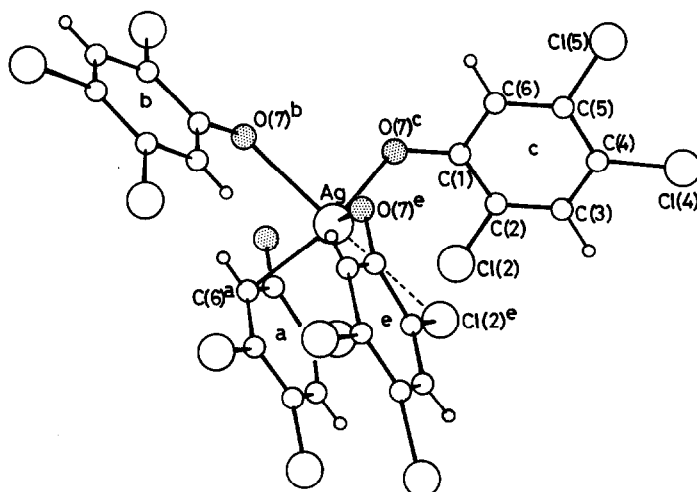


Fig. 1. Molecular configuration and atom naming scheme for silver(I) 2,4,5-trichlorophenolate.

This bonding configuration results in a symmetrical array of Ag-phenolate units which form discrete polymeric stacks, about two-fold rotational axes centred at $x, y = \pm(\frac{1}{4}, \frac{1}{4})$, extending down the c direction in the unit cell (Fig. 2). The metal-metal distances within the stacks are 3.894(1) Å ($\text{Ag}^a\text{--Ag}^b$); 3.528(1) Å ($\text{Ag}^a\text{--Ag}^c$) and 3.417(1) Å ($\text{Ag}^a\text{--Ag}^d$).

In addition to Ag-O bonds, a short symmetrical silver to ring carbon bond is found ($\text{Ag}\text{--C}(6)$, 2.443(5) Å). This completes a trigonal pyramidal stereochemistry about silver. The Ag-C distance compares with those in ethene π -bonded complexes of silver (2.41, 2.42 Å in *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene)silver(I) nitrate [10];

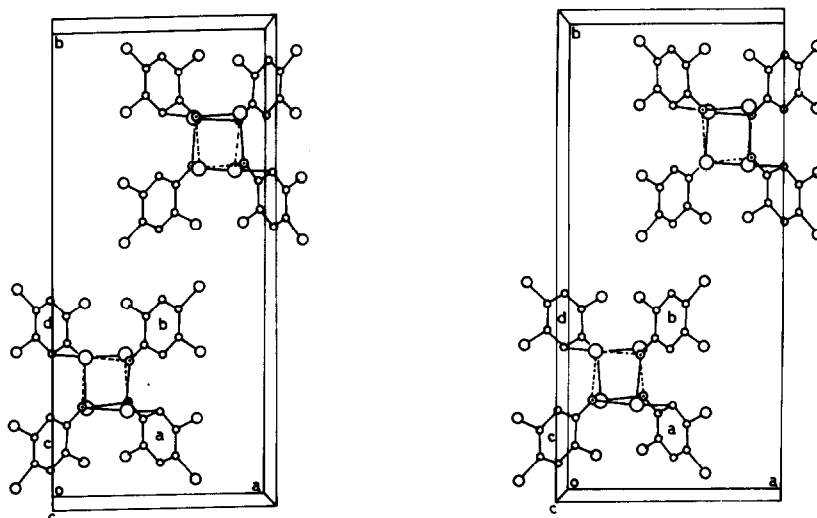


Fig. 2. Packing in the cell viewed down c .

2.49, 2.51 Å in bis(*cis*-cyclodecene)silver(I) perchlorate [11]; 2.36, 2.46 Å in inden-silver(I) perchlorate [12]). However, the important difference between these structures and that of the title compound is in the symmetry of the bond with respect to the central carbon [C(6)] (Ag–C(1), 2.907(5) Å; Ag–C(5), 2.963(5) Å; Ag–C(6)–C(1), 93.9(2)°; Ag–C(6)–C(5), 97.3(2)°; Ag–C(6)–H(6), 88(2)°). The structure is also stabilized by a Ag–Cl interaction (Ag–Cl(2)^e, 3.001(1) Å) in the approximate fifth coordination site of the trigonal bipyramid. The bonding of the phenolate ligand to silver in this complex appears to have no obvious effect upon the bond lengths within the phenyl ring. These values are very similar to those in 2,4,5-trichlorophenoxyacetic acid [13].

The only comparable example involving symmetrical Ag–C bonds is provided by [Fe(acac)₃] · AgClO₄ · H₂O [14], in which the central acac C–Ag bond is 2.29 Å.

Silver(I) 2,4,5-trichlorophenolate therefore represents a unique structure which involves both a phenolate ligand and a strong localized phenyl carbon–silver bond.

Acknowledgements

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