Crystal and Molecular Structure of Bis(1,4-benzodioxan)silver(I) Perchlorate

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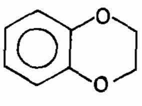
Abstract

The title compound has been shown to contain 1,4-benzodioxan with a dihapto linkage between the silver atom and the aromatic ring carbon atoms C(5) and C(6). Ag–C = 2.572(7) and 2.471(7) Å. These units are linked into chains by the perchlorate groups. Ag–O = 2.469(8) Å. The oxygen atoms of the benzodioxan are not involved in complex formation. Monoclinic, *C*2, a = 20.839(4), b = 6.990(2), c = 5.956(3) Å, β = 95.07(4)°, R = 0.043 for 1305 unique reflections.

Introduction

There is continuing interest in the complexes of salts of d(10) ions. The structure of acetonitrile [1], pyridine [2] and 1,4-oxathiane [3] complexes of silver perchlorate and copper(I) perchlorate have been reported recently. In some of these complexes the perchlorate ion is a ligand, in others it functions only as a counter-ion. Silver perchlorate is known to form a π-complex with benzene [4] and a σ-complex with 1,4-dioxan [5]. Since 1,4-benzodioxan(I) offers both possibilities the structure of the title compound was difficult to predict.



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Experimental

Equimolar ethanolic solutions of silver perchlorate and 1,4-benzodioxan were mixed and solvent removed under vacuum. Crystals suitable for X-ray study were obtained as white plates after recrystallisation from acetone. The crystals were light sensitive and unstable in air. Samples for examination were mounted in Lindemann glass capillaries. After initial oscillation and Weissenberg photographs a crystal (0.2 X 0.2 X 0.5 mm) was transferred to an Enraf-Nonus CAD4F diffractometer (SERC Service at Edinburgh University). Cell dimensions were refined from 20 accurately set reflexions with θ *ca.* 19°.

Crystallographic Data. $C_{16}H_{16}AgClO_8$. Monoclinic, *C*2, a = 20.839(4), b = 6.990(2), c = 5.956(3) Å, β = 95.07(4)°; U = 864.2 Å^3, Z = 2, $F(000)$ = 478, Dx = 1.84; Mo Kα radiation, λ = 0.71069 Å, μ = 12.4 cm^{-1}, T = 20 °C.

Data were collected for the quadrant $+h$, $+k$, $\pm l$ to a θ limit of 30°. 1356 unique reflexions were obtained of which the 1305 with $F > \sigma(F)$ were used in the refinement. During data reduction corrections were applied for absorption using a ψ scan routine, for a drift in intensity of standard reflexions of 3.0% over the 19.5 hours of the data collection and for the Lorentz and polarisation term.

All calculations were performed on the Dundee University DEC 10 computer using the SHELX 76 [6], XANADU [7] and PLUTO [8] program packages. Atomic scattering parameters were from International Tables for X-ray Crystallography (1974) [9]. Refinements minimised $\Sigma w(|Fo| - |Fc|)^2$.

The structure was solved using the direct methods routine TANG in Space Group *C*2. (The alternative space groups *Cm* and *C*2/*m* were also examined but neither gave a plausible model. The absence of a centre of symmetry was confirmed by the requirements of the final model). Structure developments by least squares refinements and difference Fourier synthesis proceeded normally. With all non hydrogen atoms included but only the silver atom given anisotropic thermal parameters R = 0.13. Including hydrogen atoms on calculated positions with grouped isotropic thermal parameters and allowing anisotropic thermal parameters for all non hydrogen atoms the refinements converged at R = 0.043.

The perchlorate oxygen atoms have unusually large thermal parameters although with positive definite ellipsoids. While the possibility of the perchlorate groups being disordered cannot be completely ruled out a refinement of the site occupancy factor for O(21) and O(22) gave a value of 0.92(2) at R = 0.043. Thus it appears that the thermal motion of these atoms is indeed large but that only a very

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TABLE Ia. Bis(1,4-benzodioxan)silver(I) Perchlorate Coordinates × 10^{-4} for non hydrogen atoms with e.s.d.s in parentheses. Ueq (A) × 10^{-3}.

	x/a	y/b	z/c	Ueq (Å)
Ag1	0	5000	5000	65(1)
Cl20	10000	7656(2)	10000	59(1)
O21	9682(7)	6630(26)	8409(24)	277(2)
O22	9513(7)	8711(17)	11018(21)	149(2)
O1	1976(2)	4011(6)	1372(7)	59(1)
C2	2427(3)	5557(10)	1714(11)	71(1)
C3	2085(4)	7266(10)	2558(13)	78(1)
O4	1866(3)	6799(8)	4758(9)	78(1)
C5	1184(3)	4671(12)	6578(7)	69(1)
C6	875(3)	2917(14)	6662(11)	81(1)
C7	907(4)	1631(11)	4983(12)	76(1)
C8	1271(3)	2017(7)	3171(10)	62(1)
C9	1554(2)	5101(10)	4792(6)	56(1)
C10	1605(2)	3734(6)	3109(7)	49(1)

TABLE Ib. Bis(1,4-benzodioxan)silver(I) Perchlorate. Anisotropic temperature factors × 10^{-3} with e.s.d.s in parentheses.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag1	47(1)	84(1)	64(1)	0	10(1)	0
Cl20	64(1)	59(1)	54(1)	0	13(1)	0
O21	113(4)	431(4)	291(4)	−303(3)	41(4)	−45(4)
O22	148(4)	120(4)	190(4)	−35(4)	76(4)	31(3)
O1	61(2)	62(2)	57(1)	−8(1)	16(1)	−5(1)
C2	63(3)	77(3)	74(2)	1(2)	14(2)	−8(2)
C3	76(3)	61(2)	94(3)	−17(2)	3(2)	−19(2)
O4	75(2)	82(2)	75(2)	−34(2)	2(2)	−16(2)
C5	59(2)	106(4)	43(1)	−8(2)	4(1)	14(2)
C6	63(2)	117(4)	66(2)	30(3)	18(2)	12(3)
C7	62(2)	76(3)	90(3)	29(2)	13(2)	5(2)
C8	58(2)	52(2)	76(2)	2(2)	12(2)	1(2)
C9	48(1)	66(2)	52(1)	−14(2)	−2(1)	7(2)
C10	45(2)	51(2)	49(2)	−2(1)	5(1)	5(1)

small fraction of the perchlorate ions can rotate onto alternative sites. There are several peaks of 0.4 e/Å or less in the final difference map at suitable distances from the chlorine atom.

Final refinement: $R = 0.043$, $wR = 0.0504$, $w = 0.2576/(\sigma(F)^2 + 0.010566\ F^2)$, mean shift/esd = 0.04, max. shift/esd = 0.153, max. difference peak 0.7 e/Å (close to Ag).

Discussion

Atomic coordinates and thermal parameters are given in Table I, with bond lengths and angles in Table II. Figure 1 shows that the structure is a chain polymer in which O(21) and O(21)′ of the perchlorate groups link silver ions which are coordinated by the 1,4-benzodioxan ligands. The Ag–O distance (2.419(8) Å) is typical of short ion–dipole or ion–ion Ag–O distances. O(22) is 3.600 Å from Ag(1) and takes no part in the first coordination sphere.

The role of the perchlorate ion in silver perchlorate complexes varies widely. In $AgClO_4\cdot3$(1,4-dioxan) [5] and $AgClO_4\cdot4CH_3CN$ [1], the perchlorate ions occupy lattice sites and take no part in the coordination. In $AgClO_4\cdot2$(1,4-oxathiane) [3] the perchlorate is coordinated by one oxygen atom in a monomeric complex with Ag–O 2.619(5) Å. The same geometry is found in the π-complex bis(cyclohexylbenzene)silver(I) perchlorate [10] where the Ag–O distance is 2.68 Å. The closest analogues to the present structure are $AgClO_4$ (benzene) which is discussed below and $AgClO_4\cdot$(1,4-thioxan) [3] which has a layer structure with Ag–O–ClO_2–O–Ag linkages at right angles to Ag–S–Ag bonds. The Ag–O distances are 2.67(4)

TABLE II. Bis(1,4-benzodioxan)silver(I) Perchlorate Interatomic Distances (Å) and Angles (°).

O21···Ag1	2.469(9)	C5–Ag1–O21	93.4(4)
C5···Ag1	2.572(6)	C6–Ag1–O21	100.6(5)
C6···Ag1	2.471(7)	C6–Ag1–C5	31.9(3)
O21···Cl20	1.319(10)	O22–Cl20–O21	104.8(9)
O22···Cl20	1.432(9)	Cl20–O21–Ag1	133.5(8)
C2···O1	1.435(7)	O21–Cl20–O21	114.1(19)
C10···O1	1.359(6)	C3–C2–O1	108.8(5)
C3···C2	1.501(11)	O4–C3–C2	108.5(6)
O4···C3	1.462(9)	C9–O4–C3	113.4(4)
C9···O4	1.354(9)	C9–C5–Ag1	106.2(3)
C6···C5	1.387(12)	C9–C5–C6	120.4(6)
C9···C5	1.400(7)	C7–C6–Ag1	100.3(4)
C7···C6	1.351(12)	C7–C6–C5	120.5(5)
C8···C7	1.399(9)	C8–C7–C6	120.6(7)
C10···C8	1.389(7)	C10–C8–C7	119.6(6)
C10···C9	1.395(6)	C5–C9–O4	119.8(5)
	C8–C10–O1	117.6(4)	
	C9–C10–O1	122.2(5)	
	C9–C10–C8	120.2(5)	

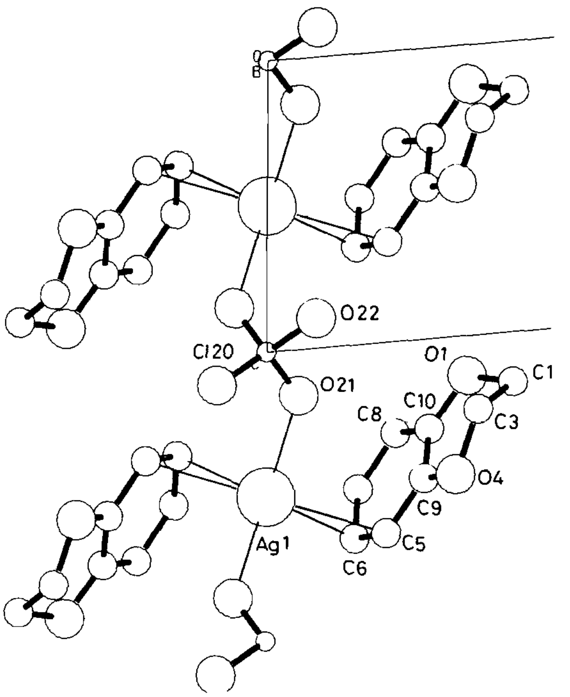

Fig. 1. Bis(1,4-benzodioxan)silver(I) perchlorate, viewed down the *b*-axis.

and 2.47(3) Å. The perchlorate oxygen atoms are ill-defined in all of these compounds, with high thermal motion and suggestions of disorder, as in the present case. Perchlorate is clearly able to compete with other ligands for sites in the inner coordination sphere of silver(I). The result of this competition is that slight variations in preparative methods often give different ratios of ligand to $AgClO_4$. For example $AgClO_4$ complexes with 1, 2 and 3 mol of (1,4-oxathiane) (tx) are all well characterised although the silver analogue of $Cu(tx)_4 \cdot ClO_4$ [3] has not been reported. Similar competition occurs with silver and nitrate; the structures of $AgNO_3 \cdot tx$, $(AgNO_3)_2 \cdot tx$ and $(AgNO_3)_6 \cdot tx$ have been reported recently [11].

The coordination of the 1,4-benzodioxan to silver is typical of that found with arenes [12]. The oxygen atoms play no part and the silver is coordinated to C(5) and C(6) only. The distances to silver are C(5) 2.572(7), C(6) 2.471(7), C(7) 3.021(8), C(8) 3.614(8), C(9) 3.253(7) and C(10) 3.728(7) Å. Thus the structure contains a π-dihapto linkage with the silver atom lying outside the area of the benzene ring. The angle between the normals to the plane of the benzene ring and the plane C(5), C(6), Ag(1) is 83.7(5)°. The angle C(5)–Ag–C(6) is 31.86(5)°. The silver atom is 6-coordinate with the coordination geometry most readily described as distorted tetrahedral by considering the C(5)–C(6) bond as a single ligand, represented by a ficticious atom D at the midpoint. Ag–D = 2.425(7) Å O(21)–Ag–D = 97.2(5), O(21)–Ag–D = 101.3(6) and O(21)–Ag–O(21) = 125.0(5)°. The angle between the normals to the planes of the two coordinated benzene rings is 47.6(5)°. It is not clear why the silver atom bonds to C(5)–C(6) rather than to C(6)–C(7). The short C(9)–O(4) and C(10)–O(1) bonds (1.357 Å average) compared with O(1)–C(2) and O(4)–C(3) (1.449 Å average) may indicate C···O interaction which would reduce both the σ-bonding ability of the ether oxygen atoms and the π-bonding ability of C(9) and C(10).

The 1,4-benzodioxan molecule has typical bond lengths and angles. C(2) and C(3) lie at 0.445(7) and –0.361(6) Å respectively from the plane of the benzene ring to give a twisted chair configuration for the dioxen ring. There are few significant differences from the dimensions of 2-(1,2-dibromoethyl)-1,4-benzodioxan recently determined in this laboratory [13] in which C(2) and C(3) lie at 0.402(5) and −0.367(5) Å from the plane. C(6)–C(7) is shorter by 0.041 Å (6σ) and C(5)–C(6) is longer by 0.018 Å (2.5σ) in the complex.

The present structure, with terminal organic ligands and bridging ClO_4 groups, lies between and $AgClO_4$(cyclohexylbenzene)$_2$ [10] which is monomeric with a planar three-coordinate silver atom with localised coordination of one bond of the benzene ring (Ag–C 2.48, 2.67 Å), and $AgClO_4$·benzene [4] where each silver atom forms a dihapto π-bond to two benzene rings with Ag–C 2.496(6) and 2.634(8) Å, C–Ag–C = 30.5°. In addition there are three contacts to perchlorate oxygen atoms at 2.68, 2.70 and 3.20 Å (both oxygen and silver sites are disordered). By accepting only the two shorter Ag–O distances the coordination geometry can be analysed as above as a very distorted tetrahedron with Ag–D = 2.479 Å, O(1)–Ag–D = 94.4, O(1)–Ag–D = 144.6 and O(1)–Ag–O(2) = 94.8°. The normal to the plane C, C, Ag makes an angle of 79.0° to the normal of the benzene ring plane. The angle between the normals to the coordinated benzene rings is 83.3°.

Variations in the C–C bond lengths around the benzene ring were reported for $AgClO_4$(benzene) and $AgClO_4$(cyclohexylbenzene)$_2$. Similar variations were seen in the present structure at R = 0.13 but these vanished as the model improved.

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