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Structure of a Polydentate Alkoxide Ligand, *cis*-Tetrahydroxytetramethylcyclobutane

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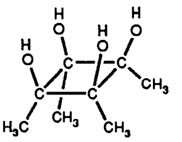
Abstract

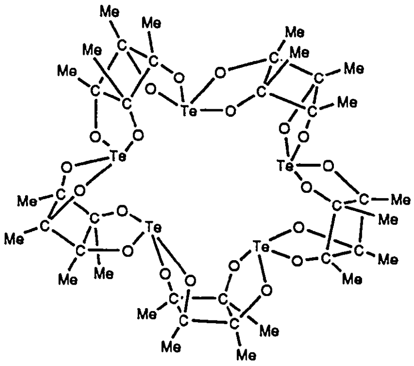
Molecules of the title compound, 1β,2β,3β,4β-tetramethylcyclobutane-1α,2α,3α,4α-tetraol, assume a layered structure with intermolecular hydrogen bonding and $CH_3\cdots CH_3$ van der Waals contacts. Some intramolecular hydrogen bonding is also observed. The cyclobutane ring is folded to the extent of 18–19° along the diagonal of the ring.

Comment

In our search for polydentate alkoxide ligands, we have identified the tetraol $Me_4C_4(OH)_4$ (1) as a candidate for the formation of a square-pyramidal complex such as $Me_4C_4O_4W{=}O$. The properties of such a complex would be of interest because there are no known complexes of a tetradentate alkoxide ligand. A complex of this unique ligand may possess unusual reactivity or be a model of metal oxide catalysis. The only known complex of (1) is a pentameric tellurane (2) in which each tetraol complexes two Te atoms in a bidentate fashion rather than in the tetradentate mode (Kahle, 1987). Reasons for this may be the preference of Te^{IV} for a 'seesaw' coordination geometry, which tetradentate (1) cannot assume, or the tendency of cyclobutanes to ring pucker [both in the solid state (Allen, 1984) and in the gas phase (Legon, 1980)]. If (1) binds as a tetradentate ligand, the degree of ring puckering may be less than in the bidentate mode.

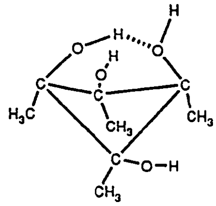


(1)



(2)

We undertook the X-ray crystal structure determination of (1) to gain insight into why the tetraol binds as in (2) and also to obtain an indication of the strength of the ring-puckering tendency in the uncomplexed ligand. In addition, the nature of the hydrogen bonding and its influence on the degree of ring puckering of uncomplexed (1) was of interest. Intramolecular hydrogen bonding between two diagonally positioned hydroxy groups of (1) might influence the degree of ring puckering because the puckering brings the hydroxy groups closer together as shown in (3).



(3)

The structure consists of bilayers of tetraol molecules having inter- and intramolecular hydrogen bonds and $CH_3\cdots CH_3$ van der Waals contacts (Fig. 2). There are two half molecules of tetraol in the asymmetric unit. One of the whole molecules is shown in Fig. 1. In each molecule, a crystallographic mirror plane passes through two O atoms and two C atoms of the four-membered ring and their two bonded methyl groups. The H atoms of the latter

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methyl groups are ordered, with one H atom in the plane and one outside it. The hydroxy H atoms are disordered between two positions (Fig. 1) in three of the four instances where the attached O atom lies in a mirror plane. Only H(6), bonded to O(6), resides in the plane. The hydroxy H atoms whose O atoms do not lie in the mirror plane are also disordered between two equally probable positions. Five possible intermolecular and two intramolecular hydrogen-bonding interactions are given in Table 3. There is generally good agreement between bond distances and most bond angles in the two molecules of (1). However, angles of the O—C—CH_3 grouping vary from 103.9 (5)° [O(6)—C(9)—C(12)] to 109.4 (5)° [O(4)—C(7)—C(10)].

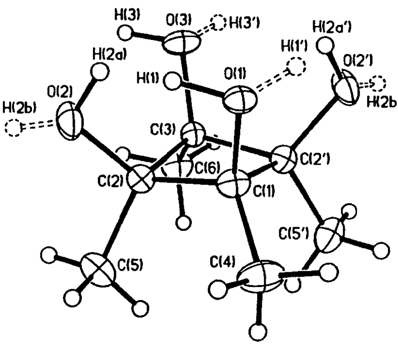

Fig. 1. One of the two molecules of (1).

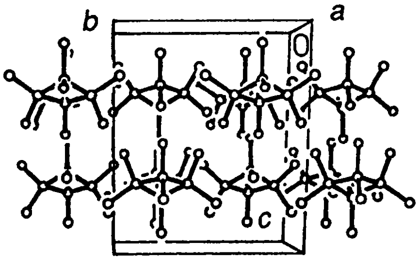

Fig. 2. Packing diagram of (1), viewed in the **a** direction.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} = 1/3(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
O(1)	0.2895 (3)	0.2500	0.6448 (3)	0.017 (1)
O(2)	0.4238 (3)	−0.0025 (3)	0.6196 (3)	0.026 (1)
O(3)	0.4842 (3)	0.2500	0.4984 (3)	0.024 (1)
C(1)	0.4260 (4)	0.2500	0.7454 (5)	0.017 (2)
C(2)	0.5079 (3)	0.1167 (4)	0.7096 (3)	0.018 (1)
C(3)	0.5641 (5)	0.2500	0.6421 (5)	0.016 (2)
C(4)	0.4211 (5)	0.2500	0.8827 (5)	0.028 (2)
C(5)	0.6147 (3)	0.0284 (5)	0.8301 (3)	0.026 (1)
C(6)	0.7125 (5)	0.2500	0.6689 (5)	0.024 (2)
O(4)	−0.0642 (4)	0.2500	0.4784 (3)	0.020 (1)
O(5)	0.1114 (2)	0.0564 (3)	0.4335 (2)	0.019 (1)
O(6)	0.2070 (3)	0.2500	0.2888 (3)	0.021 (1)
C(7)	−0.0802 (4)	0.2500	0.3405 (4)	0.014 (2)
C(8)	0.0065 (3)	0.1161 (4)	0.3107 (3)	0.014 (1)
C(9)	0.0650 (4)	0.2500	0.2463 (5)	0.016 (2)
C(10)	−0.2292 (5)	0.2500	0.2480 (5)	0.019 (2)
C(11)	−0.0637 (3)	−0.0304 (4)	0.2248 (3)	0.019 (1)
C(12)	0.0097 (5)	0.2500	0.0925 (5)	0.025 (2)

Table 2. *Bond lengths* (Å) *and angles* (°)

O(1)—C(1)	1.435 (5)	O(4)—C(7)	1.425 (6)
O(2)—C(2)	1.417 (4)	O(5)—C(8)	1.435 (3)
O(3)—C(3)	1.434 (5)	O(6)—C(9)	1.417 (6)
C(1)—C(2)	1.554 (6)	C(7)—C(8)	1.563 (5)
C(1)—C(4)	1.503 (8)	C(7)—C(10)	1.515 (6)
C(2)—C(3)	1.569 (6)	C(8)—C(9)	1.565 (6)
C(2)—C(5)	1.526 (4)	C(8)—C(11)	1.520 (4)
C(3)—C(6)	1.516 (7)	C(9)—C(12)	1.515 (7)
O(1)—C(1)—C(2)	109.3 (3)	O(4)—C(7)—C(8)	112.8 (2)
O(1)—C(1)—C(4)	107.7 (4)	O(4)—C(7)—C(10)	109.3 (4)
C(2)—C(1)—C(4)	119.9 (2)	C(8)—C(7)—C(10)	115.8 (3)
O(1)—C(1)—C(2')	109.3 (3)	O(4)—C(7)—C(8')	112.8 (2)
C(2)—C(1)—C(2')	89.5 (4)	C(8)—C(7)—C(8')	89.3 (4)
C(4)—C(1)—C(2')	119.9 (2)	C(10)—C(7)—C(8')	115.8 (3)
O(2)—C(2)—C(1)	112.5 (3)	O(5)—C(8)—C(7)	111.5 (3)
O(2)—C(2)—C(3)	115.3 (3)	O(5)—C(8)—C(9)	109.7 (3)
C(1)—C(2)—C(3)	89.6 (3)	C(7)—C(8)—C(9)	89.1 (3)
O(2)—C(2)—C(5)	108.0 (3)	O(5)—C(8)—C(11)	107.7 (3)
C(1)—C(2)—C(5)	115.8 (3)	C(7)—C(8)—C(11)	119.2 (3)
C(3)—C(2)—C(5)	115.0 (3)	C(9)—C(8)—C(11)	118.6 (3)
O(3)—C(3)—C(2)	108.9 (3)	O(6)—C(9)—C(8)	116.1 (2)
O(3)—C(3)—C(6)	109.5 (5)	O(6)—C(9)—C(12)	104.3 (4)
C(2)—C(3)—C(6)	119.7 (2)	C(8)—C(9)—C(12)	115.7 (3)
O(3)—C(3)—C(2')	108.9 (3)	O(6)—C(9)—C(8')	116.1 (2)
C(2)—C(3)—C(2')	88.5 (4)	C(8)—C(9)—C(8')	89.1 (4)
C(6)—C(3)—C(2')	119.7 (2)	C(12)—C(9)—C(8')	115.7 (3)

Symmetry code: (′) $x, \frac{1}{2} - y, z$.

Table 3. *Hydrogen-bond geometry* (Å, °)

	O—H	O···H	O···O	O—H···O
Intramolecular hydrogen bonds				
O(1)—H(1)···O(2)	0.94 (2)	1.97	2.610	125
O(2)—H(2*a*)···O(1)	0.94 (4)	2.04	2.610	117
Intermolecular hydrogen bonds				
O(5)—H(5*d*)···O(1)	0.94 (5)	2.00	2.803	141
O(3)^a—H(3)^a···O(2)	0.94 (8)	1.85	2.789	170
O(2)^a—H(2*b*)^a···O(3)	0.94 (10)	1.93	2.789	151
O(4)—H(4)···O(5)^b	0.94 (4)	1.88	2.808	166
O(5)—H(5*e*)···O(4)^c	0.94 (5)	1.87	2.808	172

Symmetry code: (*a*) $1 - x, -y, 1 - z$; (*b*) $-x, -y; 1 - z$; (*c*) $-x, y - \frac{1}{2}, 1 - z$.

The uncoordinated tetraol (1) and the coordinated tetraol in (2) differ only in the angle of pucker φ; this is defined as the complement of the dihedral angle between the two three-atom planes of the ring (Allen, 1984). Thus, φ averages 18.5 (5)° in (1) [17.7 (5)° in molecule 1, 19.3 (5)° in molecule 2] and 23.9 (4)° in (2) [range 21.3 (8)–28.3 (8)°]. Molecules 1 and 2 of (1) do not differ substantially in their degree of puckering (within experimental error). As molecule 1 contains intramolecular hydrogen bonds [as shown in (3)] while molecule 2 does not, it may be concluded that this bonding does not affect the ring puckering of (1). The considerable variation in the degree of puckering observed in the rings of (1) and (2) suggests that a number of factors may be influential; these include hydrogen bonding in (1) and the preferred geometry of the coordinated atom in (2). This suggests that puckering is not an overriding factor and that whilst it may cause some distortion of the coordination geometry, it will not necessarily prevent the formation of a square-pyramidal complex. The synthesis of molecules containing the $Me_4C_4O_4^{4-}$ unit (including $Me_4C_4O_4W{=}O$, a potentially square-pyramidal molecule) will be undertaken.

Experimental

Crystal data

$C_8H_{16}O_4$
$M_r = 176.2$
Monoclinic
$P2_1/m$
$a = 10.850\ (5)$ Å
$b = 8.206\ (4)$ Å
$c = 10.780\ (4)$ Å
$\beta = 114.07\ (3)°$
$V = 876.0\ (7)$ Å^3
$Z = 4$
$D_x = 1.34$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 35 reflections
$\theta = 8$–$20°$
$\mu = 0.099$ mm^{-1}
$T = 130$ K
Prism
0.23 × 0.10 × 0.06 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
ω scans
Absorption correction: none
1322 measured reflections
1245 independent reflections
843 observed reflections $[F>4.0\sigma(F)]$
$R_{\rm int} = 0.011$

$\theta_{\rm max} = 22.5°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 18$
$l = -11 \rightarrow 10$
2 standard reflections monitored every 198 reflections intensity variation: ±1.5%

Refinement

Refinement on F
Final $R = 0.041$
$wR = 0.049$
$S = 1.13$
843 reflections
158 parameters
$w = [\sigma^2(F)+0.0007F^2]^{-1}$

$(\Delta/\sigma)_{\rm max} = 0.06$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

The diffractometer was equipped with a modified LT-1 low-temperature apparatus and a graphite monochromator was used. Data were collected using ω scans over a 0.90° range at a scan rate of 2.00° min^{-1} and a ±0.9° offset for backgrounds. Anisotropic thermal parameters were used for all non-H atoms.

The observation of the condition $0k0$, $k = 2n$ suggested the space groups $P2_1$ or $P2_1/m$. The structure was solved and successfully refined in the latter space group.

H atoms bonded to C atoms were included at calculated positions, using a riding model with C—H 0.96 Å and fixed isotropic thermal parameters of 0.025 Å^2. Hydroxyl H atoms were located in a final difference map and refined with the additional constraint that O—H be 0.95(2) Å. Some of these were disordered; isotropic thermal parameters for such atoms were allowed to refine.

Computer programs from *SHELXTL* (Sheldrick, 1985) were used.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55246 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1001]

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Structure of the Allene $C_{39}H_{32}P_2{}^{2+}.$-$2CF_3O_3S^-$

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Abstract

In 1,3-propadienebis(triphenylphosphonium) bis(trifluoromethanesulfonate), the cation consists of two phosphane ligands which are connected by a —CH=C=CH— chain. It has point-group symmetry 2, typical of allenes. The central atom of the C_3 chain lies on the symmetry axis.

Comment

The molecule (1) was synthesized as part of a study aimed at stabilizing small molecules of formally 'naked' C atoms by complexation. It can be used to produce a molecular compound that can be considered as a C_3 chain stabilized by two phosphane ligands which act as electron donors by dehydrogenation of the two non-aromatic