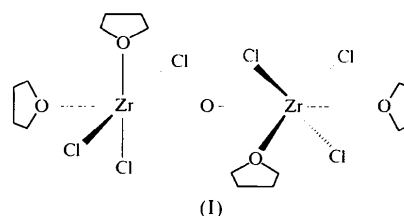


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## Comment

The title complex,  $[\text{ZrCl}_3(\text{C}_4\text{H}_8\text{O})_2]_2\text{O}$ , (I), was obtained quite unexpectedly when the reaction product of  $\text{Na}[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{OME}]$  and  $\text{C}_7\text{H}_9$  (spiro-cyclopentadienyl-[1,1']-cyclopropane) was reacted with  $\text{ZrCl}_4$  in  $\text{C}_4\text{H}_8\text{O}$  (THF). The use of carefully dried chemicals under strictly purified  $\text{N}_2$  and yields of (I) up to 20% (reference:  $\text{ZrCl}_4$ ) make it unlikely that impurities of  $\text{H}_2\text{O}$  have been the only source of the metal-bridging O atoms. Similarly, the reaction of  $\text{ZrCl}_4$  with neat 1,2-dimethoxyethane (dme) under argon was shown to afford the related complex  $[\text{ZrCl}_3(\text{dme})_2]_2\text{O}$ , (II) (Babaiian-Kibala *et al.*, 1991). However, the comparable reaction of  $\text{ZrCl}_4$  with neat THF has not yet been similarly investigated.



The crystal structure of (I) (Fig. 1) involves an uncharged dinuclear molecule, the only non-trivial symmetry element of which is a  $\text{C}_2$  axis passing through

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### $\mu$ -Oxo-bis[mer-trichlorobis(tetrahydrofuran-O)zirconium(IV)]

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## Abstract

The crystal structure of the title compound,  $[\text{ZrCl}_3(\text{C}_4\text{H}_8\text{O})_2]_2\text{O}$  or  $[\text{Zr}_2\text{Cl}_6\text{O}(\text{C}_4\text{H}_8\text{O})_4]$ , (I), was solved at room temperature and compared with that of the earlier reported complex  $[\text{ZrCl}_3(\text{MeOCH}_2\text{CH}_2\text{OME})_2]_2\text{O}$ , (II). In both molecules, two equivalent quasi-octahedral fragments involving one axial (ax) and one equatorial (eq) ether oxygen share one bridging oxide functionality. However, the point symmetry of (I) is only  $\text{C}_2$ , while that of (II) is  $\text{C}_{2h}$ . The dihedral angle of the  $\text{O}_{\text{eq}}\text{—Zr—Zr}^i\text{—O}_{\text{eq}}^i$  fragment of (I) [symmetry code: (i)  $1-x, y, \frac{1}{2}-z$ ] is  $115.3(1)^\circ$  [ $180.0^\circ$  in (II)] and the  $\text{Zr—O—Zr}^i$  angle is  $174.8(2)^\circ$  [ $180.0^\circ$  in (II)].

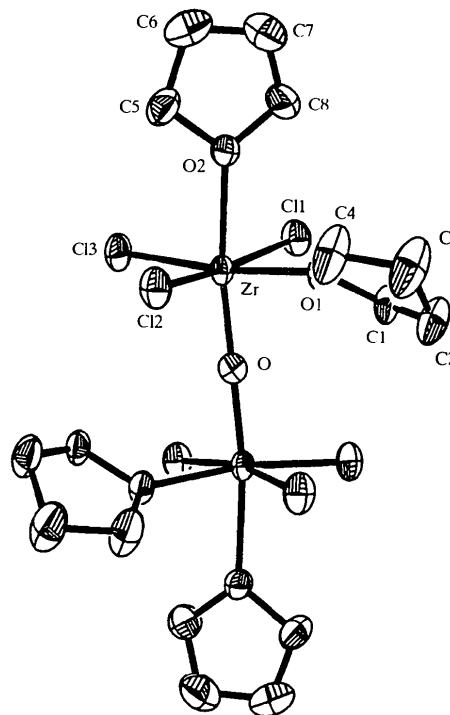


Fig. 1. The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

the bridging oxygen and bisecting *inter alia* perpendicularly the line O<sub>eq</sub>···O<sub>eq</sub><sup>i</sup> [symmetry code: (i) 1 - x, y,  $\frac{1}{2}$  - z]. Hence, although the molecule is axial chiral [the point symmetry of (I) is C<sub>2</sub>], the achiral space group implies that the crystal consists of a racemic mixture of molecules.

A perspective view of (I) (involving the THF O atoms only) along the Zr<sup>·</sup>··Zr<sup>i</sup> direction is shown in Fig. 2. The two sets of equatorial ligands (*i.e.* Cl and THF) adopt neither an eclipsed nor an ideally staggered conformation, the torsion angle of the O<sub>eq</sub>—Zr—Zr<sup>i</sup>—O<sub>eq</sub><sup>i</sup> fragment being 115.3 (1)° (Fig. 2). Corresponding dihedral angles are -72.8 (1)° from Cl1 to Cl1<sup>i</sup>, -54.0 (1)° from Cl2 to Cl2<sup>i</sup> and 120.1 (1)° from Cl3 to Cl3<sup>i</sup>. Although the Zr—μ-O distances in (I) [1.9212 (10) Å] and (II) [1.914 (1) Å] are very similar, compound (II) was shown to adopt a centrosymmetric eclipsed conformation (point group C<sub>2h</sub>). On the other hand, in (I), (II) and [ZrCl<sub>3</sub>(C<sub>4</sub>H<sub>8</sub>O)<sub>2</sub>]<sub>2</sub>(1,2-O<sub>2</sub>-c-C<sub>6</sub>H<sub>10</sub>) (Galeffi *et al.*, 1990), (III), each Zr atom carries one axial and one equatorial ether O atom. In accordance with an earlier consideration (Galeffi *et al.*, 1990), the Zr—O<sub>ax</sub> distances in (I), (II) and (III) are slightly longer than the corresponding Zr—O<sub>eq</sub> distances (Table 2). Owing to intramolecular steric congestion, most of the ligand—Zr—ligand angles in (I), (II) and (III) deviate from 90 and 180°. Apparently, the rather unexpected molecular conformation of (I) allows the most favourable packing of the molecules in the crystal (Fig. 3). A comparative

molecular modelling/force field calculation of (I) and (II) might provide further explanations for the structural differences of these two related compounds.

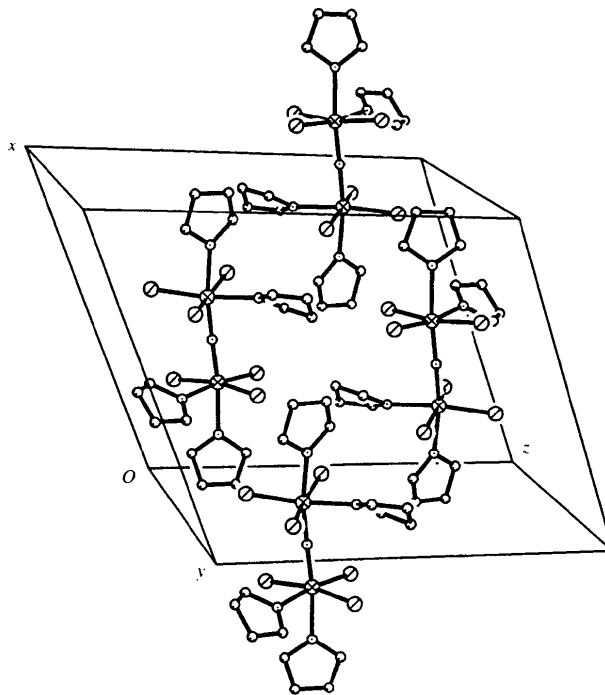


Fig. 3. Packing diagram viewed down the y axis.

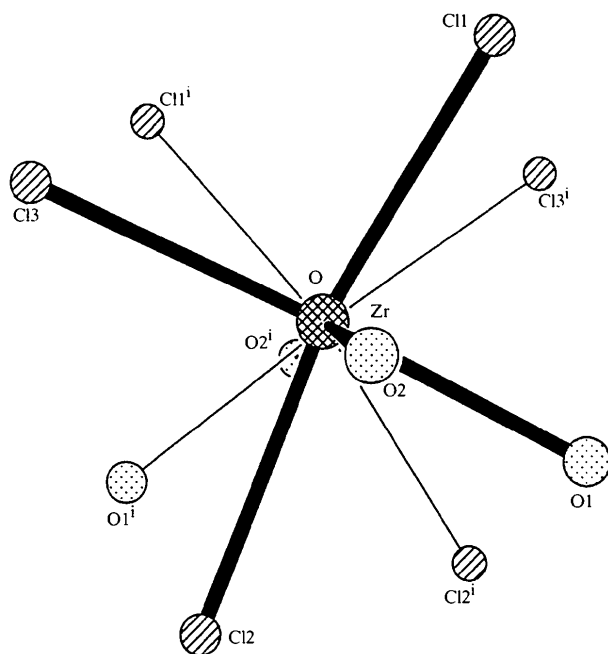


Fig. 2. The staggered conformation perspective viewed from Zr to Zr<sup>i</sup> without the C atoms of the tetrahydrofuran ligands. [Symmetry code: (i) 1 - x, y,  $\frac{1}{2}$  - z.]

## Experimental

To a suspension of ZrCl<sub>4</sub>·2THF in THF was added one equivalent each of [Na(C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>OMe)] and cyclopentadienylspiro[1,1']cyclopropane (C<sub>7</sub>H<sub>6</sub>). The mixture was stirred at ambient temperature for 12 h. The volatile components were removed and a large volume of hexane was added to the dry residue. The yellow hexane phase was separated from the heavier dark oil, concentrated slightly and cooled to 273 K whereupon colourless light-yellow crystalline needles suitable for the crystallographic study were isolated. Elemental analysis, found: C 28.1, H 4.6%; calculated for C<sub>16</sub>H<sub>32</sub>Cl<sub>6</sub>O<sub>5</sub>Zr<sub>2</sub>: C 27.5, H 4.6%.

### Crystal data

[Zr<sub>2</sub>Cl<sub>6</sub>O(C<sub>4</sub>H<sub>8</sub>O)<sub>4</sub>]

*M<sub>r</sub>* = 699.56

Monoclinic

C<sub>2</sub>/c

*a* = 15.689 (6) Å

*b* = 11.025 (6) Å

*c* = 17.641 (9) Å

β = 113.69 (7)°

*V* = 2794 (2) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.663 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 10.14–12.51°

μ = 1.342 mm<sup>-1</sup>

*T* = 293 (2) K

Needle

0.35 × 0.20 × 0.17 mm

Colourless

**Data collection**

Syntex P2 <sub>1</sub> diffractometer	$\theta_{\max} = 27.56^\circ$
$\omega$ -2 $\theta$ scans	$h = -20 \rightarrow 14$
Absorption correction: none	$k = -14 \rightarrow 12$
8427 measured reflections	$l = -22 \rightarrow 22$
3242 independent reflections	3 standard reflections
2808 reflections with $I > 4\sigma(I)$	every 100 reflections
$R_{\text{int}} = 0.053$	intensity decay: none

**Refinement**

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 1.0143P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.116$	$(\Delta/\sigma)_{\max} = -0.001$
$S = 1.241$	$\Delta\rho_{\max} = 0.58 \text{ e } \text{\AA}^{-3}$
3242 reflections	$\Delta\rho_{\min} = -1.08 \text{ e } \text{\AA}^{-3}$
133 parameters	Extinction correction: none
H-atom parameters constrained	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993a).

JG thanks the Friedrich-Ebert-Stiftung (Bonn, Germany) for a scholarship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1009). Services for accessing these data are described at the back of the journal.

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
Zr	0.36911 (2)	0.34704 (2)	0.22495 (2)	0.04290 (13)
Cl1	0.33405 (8)	0.16883 (8)	0.13446 (6)	0.0648 (2)
Cl2	0.37778 (8)	0.54499 (8)	0.29089 (6)	0.0694 (3)
Cl3	0.37036 (8)	0.23894 (9)	0.34475 (5)	0.0679 (3)
O	1/2	0.3391 (3)	1/4	0.0582 (8)
O1	0.3464 (2)	0.4559 (2)	0.11102 (13)	0.0548 (5)
O2	0.2110 (2)	0.3714 (3)	0.1764 (2)	0.0600 (6)
C1	0.3846 (3)	0.4195 (4)	0.0512 (2)	0.0630 (9)
C2	0.3866 (4)	0.5315 (5)	0.0054 (3)	0.089 (2)
C3	0.3144 (6)	0.6105 (6)	0.0131 (4)	0.125 (3)
C4	0.3109 (5)	0.5781 (5)	0.0910 (3)	0.107 (2)
C5	0.1605 (3)	0.4046 (5)	0.2271 (3)	0.0804 (12)
C6	0.0598 (4)	0.3944 (7)	0.1726 (5)	0.108 (2)
C7	0.0555 (4)	0.3818 (9)	0.0895 (4)	0.126 (3)
C8	0.1420 (4)	0.3377 (7)	0.0954 (3)	0.098 (2)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Zr—O	1.9212 (10)	Zr—Cl3	2.4194 (13)
Zr—O1	2.243 (2)	Zr—Cl1	2.4506 (13)
Zr—O2	2.292 (3)	Zr—Cl2	2.4510 (14)
O—Zr—O1	90.05 (11)	O2—Zr—Cl1	85.68 (8)
O—Zr—O2	171.03 (8)	Cl3—Zr—Cl1	95.45 (5)
O1—Zr—O2	81.02 (11)	O—Zr—Cl2	94.66 (10)
O—Zr—Cl3	98.27 (9)	O1—Zr—Cl2	84.69 (7)
O1—Zr—Cl3	171.44 (7)	O2—Zr—Cl2	85.32 (8)
O2—Zr—Cl3	90.69 (9)	Cl3—Zr—Cl2	92.56 (5)
O—Zr—Cl1	93.01 (10)	Cl1—Zr—Cl2	168.00 (4)
O1—Zr—Cl1	86.09 (8)	Zr—O—Zr <sup>†</sup>	174.8 (2)

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

H atoms were fixed at ideal positions with  $d(\text{C—H}) = 0.97 \text{ \AA}$  and with a common isotropic displacement parameter ( $U_{\text{iso}} = 0.15 \text{ \AA}^2$ ). All crystallographic calculations were carried using *SHELXL93* (Sheldrick, 1993a) and *SHELXTL-Plus* (Sheldrick, 1993b). The largest residue peak ( $1.08 \text{ e } \text{\AA}^{-3}$ ) lay close to the heavy Zr atom in the final cycle of refinement. The C7—C8 distance is clearly shorter than the normal  $\text{Csp}^3\text{—Csp}^3$  bond length; this may be due to the strong thermal motion of the C atoms in the THF molecule.

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### [N,N'-Bis(5-methoxysalicylidene)-1,2-diphenyl-1,2-ethenediamine]-oxovanadium(IV)†

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**Abstract**

The title complex,  $[\text{VO}(\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_4)]$ , adopts a monomeric structure in the crystals, which are red due to the charge-transfer band from the conjugated  $\pi$ -system of the tetradentate Schiff base ligand. The geometry around the  $\text{V}^{\text{IV}}$  atom is distorted square pyramidal. The  $\text{V}=\text{O}$  distance is  $1.588(3) \text{ \AA}$ , and the V atom is displaced by  $0.57(1) \text{ \AA}$  from the  $\text{N}_2\text{O}_2$  coordination plane towards the apical oxo ligand.

**Comment**

Upon heating at 483 K, the green powder of  $[\text{VO}(5\text{-MeOsal-meso-stien})]$  [ $\text{H}_2(5\text{-MeOsal-meso-stien})$ ]

† Alternative name: {4,4'-dimethoxy-2,2'-[1,2-diphenylethene-1,2-diy]bis(nitrimethylidyne)}diphenolato-*O,N,N',O'*oxovanadium(IV).