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Key indicators

Single-crystal X-ray study
T = 183 K
Mean $\sigma(\text{C}-\text{C}) = 0.013 \text{ \AA}$
R factor = 0.039
wR factor = 0.106
Data-to-parameter ratio = 10.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Di- μ -hydroxo- $\kappa^4\text{O}:\text{O}$ -bis[aquatris(triphenylsilanolato- κO)zirconium(IV)] toluene solvate

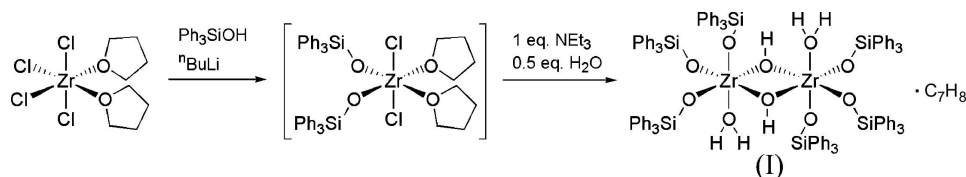
The title compound, $[\text{Zr}_2(\text{C}_{18}\text{H}_{15}\text{OSi})_6(\text{OH})_2(\text{H}_2\text{O})_2] \cdot \text{C}_7\text{H}_8$, is a dimeric Zr^{IV} compound. The asymmetric unit consists of two half-molecules of the complex and a toluene solvent molecule. The zirconium centres are bridged by two μ -hydroxo ligands. Each Zr is octahedrally coordinated by the hydroxo groups, three triphenylsilanolato groups and an additional water ligand. The centres of both Zr_2O_2 rings are located on crystallographic centres of inversion. The two independent monomeric units differ significantly with respect to the Zr—O—Si bond angles which is most probably due to the high steric demands of three triphenylsilanolato ligands.

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Comment

The extraordinary potential of metallocene-type group 4 metal catalysts in olefin oligomerization or polymerization has been intensively studied in terms of the promotion of highly active cationic species by methylalumoxan (MAO), the isolation of these cationic species themselves, the development of so-called 'single-site' catalysts and the adjustment of ligands in order to achieve highly selective catalytic reactions (Brintzinger *et al.*, 1995; Britovsek *et al.*, 1999; Möhring & Coville, 1994; Bochmann, 1996; Kaminsky, 1996; Erker *et al.*, 2004; Cotton, 2000; Kaminsky, 2000; Chirik & Bercaw, 2000; Piers *et al.*, 1999; Chien, 1999; Alt & Samuel, 1998). The chemistry of group 4 metal complexes containing inorganic donor sets, *viz.* O or N donor sites, is much less developed because the coordination chemistry of these compounds is much more complicated than that of metallocene derivatives (Britovsek *et al.*, 1999; Tajima & Kunioka, 1968; Gibson *et al.*, 1998; Shah *et al.*, 1996; Horton & de With, 1996; Tinkler *et al.*, 1996; Baumann *et al.*, 1997; Scollard & McConville, 1996; Walther *et al.*, 1996; Sobota *et al.*, 1997; Floriani *et al.*, 1989; North *et al.*, 1998; Solari *et al.*, 1992; Schweder, Walther *et al.*, 1999; Murugavel *et al.*, 1996).



In the course of our investigations on the synthesis, structural properties and catalytic activity of bis-silanolato- Zr^{IV} complexes, which are easily accessible from $\text{ZrCl}_4(\text{THF})_2$ and the corresponding deprotonated silanols (THF is tetrahydrofuran; see scheme), in Ziegler–Natta systems (Schweder, Görls

& Walther, 1999), we became interested in the structures of tris-silanolato-Zr^{IV} compounds. By carrying out the hydrolysis of the intermediate [ZrCl₂(THF)₂(Ph₃SiO)₂] with an exact amount of water (0.5 equivalent) in the presence of NEt₃ to avoid acidic conditions during the reaction, several products were obtained. As a minor product the title compound could be isolated as colourless crystals suitable for X-ray diffraction during the work-up procedure. Compounds related to the title compound may be considered as molecular models for catalytically active Zr^{IV} centres at silica surfaces, as the first species in hydrolytic reactions in sol-gel processes or as precursors in aggregation reactions. The typical molecular chemistry of this class of compounds has been thoroughly reviewed before (Murugavel *et al.*, 1996).

The molecular structure of the title compound is presented in Fig. 1. The dimeric structure is built up by two μ -hydroxo ligands bridging the Zr atoms and thus producing a Zr₂O₂ ring. The centre of this four-membered ring is located on a crystallographic centre of inversion, so that only half of the molecule is observed in the asymmetric unit. However, the crystal structure showed the presence of two symmetry-independent monomeric units. The zirconium centres are octahedrally coordinated by six oxygen donor ligands. The three triphenylsilanolato ligands are arranged in a facial configuration. The assignment of the bridging O atoms to represent hydroxo ligands and the η^1 -coordinated O atom to be a water ligand is justified for two reasons. Firstly, the neutral water ligands show much longer Zr—O bond lengths [Zr1—O5 = 2.329 (3) Å and Zr2—O10 2.328 (3) Å] compared with the corresponding distances of the negatively charged OH groups to Zr (Table 1). Furthermore, all H atoms of the hydroxo as well as the water ligands were found in a difference Fourier map. The Zr atoms are situated above the plane consisting of the two μ -hydroxo O atoms and two of the silanolato ligands. The deviation of Zr1 from the least-squares plane through atoms O2, O3, O4 and O4ⁱ [symmetry code: (i) 1 - x, 2 - y, 1 - z] is 0.301 (1) Å, whereas Zr2 is observed 0.257 (1) Å above the corresponding plane through atoms O7, O8, O9 and O9ⁱⁱ [symmetry code (ii) 1 - x, 1 - y, -z]. In order to avoid steric crowding the axially coordinated silanolato ligands are bent out of a perpendicular arrangement with respect to the central Zr₂Cl₂ ring [Zr1A—Zr1—O1 = 98.22 (9)°, Zr2A—Zr2—O6 = 94.71 (9)°]. The structural motif [(RO)₃(H₂O)Zr(μ -OH)₂Zr(H₂O)(OR)₃] is virtually identical in both dimeric complexes observed in the crystal structure. Nevertheless, there are significant differences in the Zr—O—Si bond angles (Table 1). These differences are most probably caused by packing effects due to the high steric demands of the triphenylsilanolato groups. Highly related compounds with a dimeric Zr₂(μ -OR)₂ unit exhibiting three alcoholates and one η^1 -coordinated alcohol as the additional ligands at each zirconium have been structurally characterized for 2-propanol (Seisenbaeva *et al.*, 2004; Vaartstra *et al.*, 1990; Boyle *et al.*, 1995; Imam & Rao, 1963). In all these structures the bridging ligands also are alcoholates. There are also examples in which one of the alcoholates and the neutral alcohol ligand are replaced by an anionic bidentate ligand, such as 1,3-diketo-

nates (Seisenbaeva *et al.*, 2004; Fleeting *et al.*, 1999; Patil *et al.*, 2003), aryloxides (Evans *et al.*, 1999) or phosphonates (Chakraborty *et al.*, 2000). Nevertheless, in the latter compounds also, alcoholates occupy the bridging positions between the zirconium centres. There is only one OH-bridged dimeric Zr^{IV} complex structurally characterized up to now, in which the ligand coordination around each of the Zr atoms is completed by one cyclopentadienyl ligand and two nitrate ions acting as bidentate ligands (Lasser & Thewalt, 1984).

Experimental

A solution of triphenylsilanol (2.40 g, 8.69 mmol) in THF (20 ml) at 253 K was treated with a 1.6 molar solution (5.44 ml) of BuLi in THF. After 15 min, [ZrCl₄(THF)₂] (1.64 g, 4.34 mmol) in THF (20 ml) was added. To the resulting clear colourless solution containing [ZrCl₂(THF)₂(Ph₃SiO)₂] a mixture of NEt₃ (0.7 ml, 5.0 mmol) and water (39 μ l, 2.17 mmol, 0.5 equivalents) in THF (5 ml) was added. The mixture was allowed to reach room temperature and was stirred at 298 K for an additional hour. From the resulting colourless suspension all volatile material was removed *in vacuo* and the residue was suspended in CH₂Cl₂ (20 ml). After filtration, the solvent was removed *in vacuo* and the resulting white solid was treated with toluene (20 ml), leading to a cloudy solution which again was filtered. The slightly yellow filtrate was layered with *n*-hexane (10 ml) and stored at 298 K. After two days, a precipitate of another compound had formed, which was filtered off. Layering the resulting solution again with (15 ml) *n*-hexane led to the isolation of colourless crystals (0.08 g, 9.2%) of the title compound. The title compound may also be obtained from the reaction of *in situ* prepared [ZrCl₂(THF)₂(Ph₃SiO)₂] with Li₂O/water and a similar work-up procedure. ¹H NMR (298 K, CD₂Cl₂, p.p.m.): 2.39 (s, 1.5H, CH₃), 3.58 (m, 6H, H₂O/OH), 6.94–7.67 (m, 94, CH_{ar}); IR (298 K, Nujol, cm⁻¹): 3556, 3065, 3047, 1587, 1115, 1027, 997, 927, 866, 740, 708, 699, 517; Elemental analysis for C₁₀₈H₉₆O₁₀Si₆Zr₂ × 0.5 toluene found: C 67.05, H 5.45%; calculated: C 68.64, H 5.17%.

Crystal data

[Zr ₂ (C ₁₈ H ₁₅ OSi) ₆ (OH) ₂ ·(H ₂ O) ₂ ·C ₇ H ₈]	Z = 2
<i>M_r</i> = 1996.96	<i>D_x</i> = 1.283 Mg m ⁻³
Triclinic, P $\bar{1}$	Mo K α radiation
<i>a</i> = 14.693 (4) Å	Cell parameters from 25 reflections
<i>b</i> = 16.324 (3) Å	θ = 8.3–14.5°
<i>c</i> = 24.794 (4) Å	μ = 0.33 mm ⁻¹
α = 90.08 (1)°	<i>T</i> = 183 (2) K
β = 105.32 (2)°	Cuboid, colourless
γ = 114.70 (2)°	0.05 × 0.04 × 0.04 mm
<i>V</i> = 5168 (2) Å ³	

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> _{int} = 0.016
$\omega/2\theta$ scans	θ _{max} = 20.6°
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	<i>h</i> = -14 → 14
<i>T</i> _{min} = 0.925, <i>T</i> _{max} = 0.988	<i>k</i> = -16 → 16
10711 measured reflections	<i>l</i> = -24 → 0
10400 independent reflections	3 standard reflections
9107 reflections with <i>I</i> > 2 σ (<i>I</i>)	frequency: 600 min
	intensity decay: 0.9%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.106$
 $S = 1.05$
 10400 reflections
 971 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 9.3505P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Zr1—O3	1.967 (3)	Zr2—O8	1.954 (3)
Zr1—O1	1.970 (3)	Zr2—O6	1.958 (3)
Zr1—O2	1.974 (3)	Zr2—O7	1.964 (3)
Zr1—O4	2.133 (3)	Zr2—O9	2.210 (3)
Zr1—O4 ⁱ	2.174 (3)	Zr2—O9 ⁱⁱ	2.227 (3)
Zr1—O5	2.329 (3)	Zr2—O10	2.328 (3)
O1—Si1	1.617 (3)	O6—Si4	1.621 (3)
O2—Si2	1.621 (3)	O7—Si5	1.613 (3)
O3—Si3	1.618 (3)	O8—Si6	1.617 (3)
O3—Zr1—O1	100.27 (11)	O8—Zr2—O6	99.13 (13)
O3—Zr1—O2	100.74 (11)	O8—Zr2—O7	102.30 (13)
O1—Zr1—O2	99.31 (11)	O6—Zr2—O7	100.24 (12)
O3—Zr1—O4	153.66 (11)	O8—Zr2—O9	92.52 (12)
O1—Zr1—O4	96.26 (11)	O6—Zr2—O9	95.46 (11)
O2—Zr1—O4	96.62 (10)	O7—Zr2—O9	156.30 (11)
O3—Zr1—O4 ⁱ	88.58 (10)	O8—Zr2—O9 ⁱⁱ	161.33 (12)
O1—Zr1—O4 ⁱ	97.28 (11)	O6—Zr2—O9 ⁱⁱ	92.19 (12)
O2—Zr1—O4 ⁱ	159.15 (10)	O7—Zr2—O9 ⁱⁱ	90.12 (12)
O4—Zr1—O4 ⁱ	68.98 (11)	O9—Zr2—O9 ⁱⁱ	71.54 (13)
O3—Zr1—O5	82.28 (11)	O8—Zr2—O10	86.43 (12)
O1—Zr1—O5	175.30 (12)	O6—Zr2—O10	172.72 (12)
O2—Zr1—O5	84.01 (11)	O7—Zr2—O10	83.02 (12)
O4—Zr1—O5	80.00 (12)	O9—Zr2—O10	79.52 (11)
O4 ⁱ —Zr1—O5	78.78 (11)	O9 ⁱⁱ —Zr2—O10	81.26 (11)
Si1—O1—Zr1	169.22 (18)	Si4—O6—Zr2	168.6 (2)
Si2—O2—Zr1	159.77 (16)	Si5—O7—Zr2	170.06 (19)
Si3—O3—Zr1	158.70 (17)	Si6—O8—Zr2	176.1 (2)
Zr1—O4—Zr1 ⁱ	111.02 (11)	Zr2—O9—Zr2 ⁱⁱ	108.46 (13)

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z$.

All H atoms of the phenyl groups and the methyl substituent of toluene were placed in idealized positions ($C-H = 0.95$ and 0.98 \AA) and their isotropic displacement parameters were set to 1.2 or 1.5 of those of the parent atom. The H atoms of the hydroxo groups (O4 and O9) and water ligands (O5 and O10) were found in a difference Fourier map. Nevertheless, during the final refinement both coordinates and displacement parameters were constrained [$O-H = 0.92-0.99 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5-1.7U_{\text{eq}}(\text{O})$]. All six-membered rings were constrained to ideal hexagons.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *MolEN* (Nonius, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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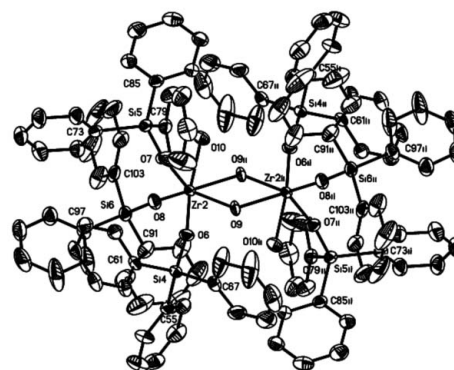
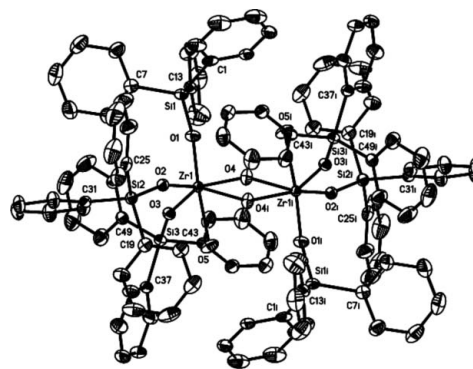


Figure 1

Molecular structures of the two independent molecules of the title compound [symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$]. H atoms and the solvent molecule have been omitted for clarity. Displacement parameters are drawn at the 30% probability level.

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