

Zirconium tetrachloride revisited

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Zirconium tetrachloride, $ZrCl_4$, is a strategic material with wide-ranging applications. Until now, only one crystallographic study on $ZrCl_4$ has been reported [Krebs (1970). *Z. Anorg. Allg. Chem.* **378**, 263–272] and that was more than 40 years ago. The compound used for the previous determination was prepared from ZrO_2 and Cl_2-CCl_4 , and single-crystal X-ray diffraction (SCXRD) studies on $ZrCl_4$ obtained from Zr metal have not yet been reported. In this context, we prepared $ZrCl_4$ from the reaction of Zr metal and Cl_2 gas in a sealed tube and investigated its structure at 100, 150, 200, 250, and 300 K. At 300 K, the SCXRD analysis indicates that $ZrCl_4$ crystallizes in the orthorhombic space group $Pca2_1$ [$a = 6.262$ (9), $b = 7.402$ (11), $c = 12.039$ (17) Å, and $V = 558.0$ (14) Å³] and consists of infinite zigzag chains of edge-sharing $ZrCl_6$ octahedra. This chain motif is similar to that observed previously in $ZrCl_4$, but the structural parameters and space group differ. In the temperature range 100–300 K, no phase transformation was identified, while elongation of intra-chain $Zr \cdots Zr$ [3.950 (1) Å at 100 K and 3.968 (5) Å at 300 K] and inter-chain $Cl \cdots Cl$ [3.630 (3) Å at 100 K and 3.687 (9) Å at 300 K] distances occurred.

1. Introduction

Zirconium tetrachloride is an important material with a variety of industrial applications. It is used in the Kroll process as a precursor to metallic zirconium (Lustman & Kerze, 1955), as a catalyst in organic synthesis pathways (Bora, 2003; Li *et al.*, 2006; Sharma *et al.*, 2003), and for chemical-vapor deposition (Randich, 1979). It is also encountered in nuclear applications for the recycling of zirconium cladding using a chloride volatility process (Bohe *et al.*, 1996; Collins *et al.*, 2012; Min Ku *et al.*, 2013).

Zirconium tetrachloride can be synthesized from the direct reaction between Zr metal and Cl_2 gas at high temperatures (>623 K) (Collins *et al.*, 2012), or from the treatment of ZrO_2 with CCl_4 or Cl_2 gas in the presence of carbon (Hermann, 1844). Zirconium tetrachloride is a very reactive material, it is hygroscopic and reacts rapidly with air to form zirconium oxychloride hydrates; therefore, special care is needed to prepare and handle this material. In view of its air sensitivity, few solid-state chemistry studies on $ZrCl_4$ have been reported and the preparation and handling of $ZrCl_4$ single crystals suitable for X-ray diffraction is a challenging task. In the solid state, $ZrCl_4$ has been characterized by vibrational spectroscopy (Salyulev & Vovkotrub, 2013; Weidlein *et al.*, 1968) and single-crystal X-ray diffraction (SCXRD).

There has been only one SCXRD study on $ZrCl_4$, which dates from the 1970s (Krebs, 1969, 1970). It was shown that $ZrCl_4$ crystallizes in the monoclinic space group $P2_1/c$ and adopts a zigzag chain structure consisting of edge-sharing

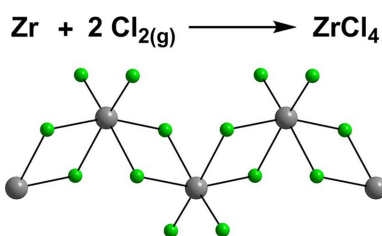


Table 1
Experimental details.

For all determinations, the chemical formula and M_r were $ZrCl_4$ and 233.02, respectively, the crystal system and space group were orthorhombic $Pca2_1$, the diffractometer used was a Bruker D8 QUEST, and a numerical absorption correction was applied (*SADABS*; Krause *et al.*, 2015).

	ZrCl ₄ at 100 K	ZrCl ₄ at 150 K	ZrCl ₄ at 200 K
Crystal data			
Temperature (K)	100	150	200
a, b, c (Å)	6.2199 (9), 7.3301 (10), 11.9153 (16)	6.2311 (8), 7.3497 (10), 11.9462 (15)	6.2389 (8), 7.3667 (10), 11.9735 (16)
V (Å ³)	543.25 (13)	547.10 (12)	550.30 (13)
Z	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	3.82	3.79	3.77
Crystal size (mm)	0.09 × 0.08 × 0.06	0.09 × 0.08 × 0.06	0.09 × 0.08 × 0.06
Data collection			
T_{\min}, T_{\max}	0.63, 0.81	0.64, 0.78	0.64, 0.82
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5240, 924, 877	5124, 906, 853	5292, 934, 864
R_{int}	0.050	0.051	0.049
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.588	0.588	0.588
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.084, 1.07	0.033, 0.080, 1.04	0.038, 0.095, 1.11
No. of reflections	924	906	934
No. of parameters	46	46	46
No. of restraints	1	1	1
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	2.08, -0.53	2.08, -0.52	2.11, -0.54
Absolute structure	Flack x determined using 394 quotients $[(I^+) - (I^-)]/$ $[(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)	Flack x determined using 374 quotients $[(I^+) - (I^-)]/$ $[(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)	Flack x determined using 386 quotients $[(I^+) - (I^-)]/$ $[(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	-0.05 (15)	-0.03 (14)	0.18 (17)
<hr/>			
	ZrCl ₄ at 250 K	ZrCl ₄ at 300 K	
Crystal data			
Temperature (K)	250	300	
a, b, c (Å)	6.253 (5), 7.383 (6), 12.017 (9)	6.262 (9), 7.402 (11), 12.039 (17)	
V (Å ³)	554.8 (7)	558.0 (14)	
Z	4	4	
Radiation type	Mo $K\alpha$	Mo $K\alpha$	
μ (mm ⁻¹)	3.74	3.71	
Crystal size (mm)	0.09 × 0.08 × 0.06	0.09 × 0.08 × 0.06	
Data collection			
T_{\min}, T_{\max}	0.63, 0.81	0.55, 0.81	
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5285, 934, 815	5334, 949, 737	
R_{int}	0.063	0.093	
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.588	0.588	
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.096, 1.05	0.053, 0.138, 1.02	
No. of reflections	934	949	
No. of parameters	46	46	
No. of restraints	1	1	
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	2.13, -0.48	2.59, -0.70	
Absolute structure	Flack x determined using 351 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)	Flack x determined using 284 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)	
Absolute structure parameter	0.01 (15)	0.0 (3)	

Computer programs: *BIS* (Bruker, 2016), *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2015), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *shelXle* (Hübschle *et al.*, 2011).

ZrCl₆ octahedra (Krebs, 1970). The method used to prepare ZrCl₄ involved the reaction of ZrO₂ with Cl₂ + CCl₄ in the temperature range 773–973 K; but the synthetic procedure (mass, reaction time, ramping temperature rate, annealing time) was not reported. It was mentioned that the SCXRD measurement was performed at 293 K, but the uncertainty on

the temperature was not reported. Because, ZrCl₄ will be produced from the reaction of Zr metal and Cl₂ in zirconium cladding reprocessing, the investigation of the structure of ZrCl₄ prepared from Zr metal is of importance; it will be of interest to compare the structure of ZrCl₄ obtained from ZrO₂ and that from Zr metal.

Table 2

Unit-cell parameters (Å), volume (Å³), and selected bond lengths (Å) and angles (°) in ZrCl₄ obtained here and by Krebs (1970).

	Present work	Krebs (1970)
Cl(bri1), Cl(bri2) and Cl(ter) represent the bridging and terminal Cl ligands.		
Space group	<i>Pca</i> 2 ₁	<i>P2</i> / <i>c</i>
<i>Z</i>	4	2
<i>T</i> (K)	300	293
<i>a</i> (Å)	6.262 (9)	6.361 (4)
<i>b</i> (Å)	7.402 (11)	7.407 (4)
<i>c</i> (Å)	12.039 (17)	6.256 (4)
$\alpha/\beta/\gamma$ (°)	90/90/90	90/109.30 (4)/90
<i>V</i> (Å ³)	558.0 (14)	278.2
Avg. Zr1—Cl(ter)	2.312	2.307
Avg. Zr1—Cl(bri2)	2.504	2.498
Avg. Zr1—Cl(bri1)	2.667	2.655
Zr1···Zr1 ⁱⁱ	3.965 (1)	3.962 (2)
Cl1—Zr1—Cl3	100.6 (2)	100.7 (1)
Cl1—Zr1—Cl4	98.73 (19)	98.5 (1)
Cl2—Zr1—Cl3	98.5 (2)	
Cl4—Zr1—Cl2 ⁱⁱ	79.89 (16)	79.5 (1)
Cl4—Zr1 ⁱⁱ —Cl2 ⁱⁱ	79.76 (16)	
Cl2 ⁱⁱ —Zr1—Cl4 ⁱ	81.54 (17)	81.5 (1)
Cl2—Zr1—Cl4	160.82 (17)	160.7 (1)
Cl1—Zr1—Cl4 ⁱ	168.9 (2)	168.9 (1)
Cl3—Zr1—Cl2 ⁱⁱ	168.9 (2)	
Cl4—Zr1—Cl3	93.3 (2)	93.8 (1)
Cl2—Zr1—Cl1	93.9 (2)	

Considering the strategic importance of ZrCl₄, the re-determination of its crystallographic structure at various temperatures is also needed. Obtaining accurate structural data on ZrCl₄ in various ranges of temperature will help theoreticians prove the accuracy of their theoretical model. In this study, ZrCl₄ was prepared from the reaction of Zr metal and Cl₂ gas in a sealed tube and its structure investigated by SCXRD at 100, 150, 200, 250, and 300 K.

2. Experimental

Zirconium metal (>99% purity) and a lecture bottle of chlorine gas (>99.5% purity) were obtained from Sigma–Aldrich and used as received. The clamshell furnace was a Lindberg Blue M Mini-Mite equipped with a temperature control.

2.1. Synthesis and crystallization

Zirconium tetrachloride was synthesized from the reaction of Zr metal and chlorine gas in a sealed glass tube. The method is similar to that reported for the preparation of technetium tetrachloride (Johnstone *et al.*, 2012). In a typical preparation, zirconium metal (20 mg, 0.22 mmol) was placed in a Pyrex tube (internal diameter = 8 mm and length = 30 cm) connected to a Schlenk line and flamed under vacuum. After backfilling with chlorine gas, the end of the tube was cooled in liquid nitrogen and ~0.65 mmol of Cl₂ were condensed (Zr:Cl ~1:6). The tube was flame sealed (length = 25 cm after sealing) and placed in a clamshell furnace. The temperature was increased to 573 K (at a rate of 10 K min⁻¹) and held for 6 h at this temperature. After cooling to room temperature, a nonvolatile material (probably zirconium oxide) was observed at the end

Table 3

Selected bond lengths (Å) in ZrCl₄ at 100, 150, 200, 250, and 300 K.

	300 K	250 K	200 K	150 K	100 K
Zr—Cl1	2.313 (6)	2.315 (4)	2.309 (3)	2.314 (3)	2.314 (3)
Zr1—Cl2	2.504 (6)	2.501 (4)	2.499 (3)	2.497 (2)	2.497 (3)
Zr1—Cl3	2.310 (6)	2.311 (4)	2.316 (3)	2.313 (3)	2.313 (3)
Zr1—Cl4	2.504 (6)	2.501 (4)	2.503 (3)	2.501 (2)	2.499 (2)
Zr1—Cl2 ⁱⁱ	2.664 (5)	2.662 (4)	2.661 (3)	2.660 (3)	2.659 (3)
Zr1—Cl4 ⁱ	2.670 (5)	2.667 (3)	2.662 (3)	2.663 (2)	2.659 (2)
Zr1···Zr1 ⁱⁱ	3.968 (5)	3.964 (3)	3.958 (1)	3.957 (1)	3.950 (1)
Avg. Zr1—Cl(ter)	2.312 [6]	2.313 [4]	2.313 [5]	2.314 [3]	2.314 [3]
Avg. Zr1—Cl(bri2)	2.504 [6]	2.501 [4]	2.501 [3]	2.499 [2]	2.498 [3]
Avg. Zr1—Cl(bri1)	2.667 [5]	2.665 [4]	2.662 [3]	2.662 [3]	2.659 [3]
Cl1···Cl3*	3.687 (9)	3.679 (5)	3.658 (5)	3.647 (3)	3.630 (3)

Symmetry codes: (i) $x - \frac{1}{2}, -y + 1, z$; (ii) $x + \frac{1}{2}, -y + 1, z$; (*) $-x + \frac{1}{2}, y, z + \frac{1}{2}$ (interchain distance).

of the tube containing the metal, while a white solid (ZrCl₄) was present at the cold end. After the reaction, the end of the tube containing the volatile compound was placed in liquid nitrogen and the tube was sealed at 18 cm, thus removing the zirconium oxide. The tube containing ZrCl₄ was wrapped in aluminium foil and the entire tube was placed in the clamshell furnace. The temperature was increased to 428 K (at a rate of 0.3 K min⁻¹) and held for 96 h at this temperature. After cooling to room temperature (at a rate of 0.3 K min⁻¹), white prismatic crystals were present on the surface near the middle of the tube, and these were used for the SCXRD study.

2.2. Sample handling

The sealed tube containing the ZrCl₄ crystals was broken using a glass cutter. The colorless prismatic crystals were immediately placed in fluorinated oil (DuPont Krytox GPL106). In the absence of oil, decomposition of the crystal was observed immediately (evolution of HCl gas). In the fluorinated oil, the crystals are stable at room temperature for at least 4 h. A suitable crystal was selected and mounted under the fluorinated oil on a MiTeGen Micromount. The time between the opening of the Pyrex tube and the mounting of the ZrCl₄ crystal on the diffractometer was 20 min.

2.3. Refinement

The crystal data and refinement quality factors for ZrCl₄ from 100 to 300 K are presented in Table 1, together with the data collection and structure refinement details. The apparent space group for the structure at all five temperatures was suggested to be orthorhombic *Pca*2₁ by *XPREP* (Bruker, 2016), which differs from that previously described, *i.e.* monoclinic *P2*/*c* (Krebs, 1970) (Table 2). The residual electron density in each structure is around 2 e Å⁻³ and is located between the Zr1 and Cl4 atoms. Therefore, it cannot be assigned to any atoms, such as oxygen from water or chlorine/hydrogen from hydrogen chloride.

3. Results and discussion

The effect of temperature on the ZrCl₄ structural parameters was evaluated between 100 and 300 K. Analyses of the

Table 4
Selected bond angles (°) in ZrCl₄ at 100, 150, 200, 250, and 300 K.

	300 K	250 K	200 K	150 K	100 K
Cl1—Zr1—Cl3	100.6 (2)	100.76 (13)	100.74 (11)	100.76 (9)	100.75 (9)
Cl1—Zr1—Cl4	98.73 (19)	98.47 (12)	98.49 (10)	98.39 (9)	98.34 (9)
Cl2 ⁱⁱ —Zr1—Cl4 ⁱ	81.54 (17)	81.41 (11)	81.36 (8)	81.27 (7)	81.26 (7)
Cl2—Zr1—Cl3	98.5 (2)	98.46 (13)	98.37 (11)	98.31 (9)	98.17 (9)
Cl2—Zr1—Cl4	160.82 (17)	160.79 (11)	160.72 (10)	160.69 (9)	160.75 (9)
Zr1—Cl4—Zr1 ⁱⁱ	100.08 (19)	100.12 (12)	100.02 (10)	99.96 (9)	99.90 (9)
Zr1—Cl2 ⁱⁱ —Zr1 ⁱⁱ	100.26 (19)	100.26 (12)	100.16 (11)	100.15 (9)	99.96 (9)
Cl4—Zr1—Cl2 ⁱⁱ	79.89 (16)	79.85 (10)	79.87 (9)	79.93 (7)	80.05 (7)
Cl4—Zr1 ⁱⁱ —Cl2 ⁱⁱ	79.76 (16)	79.76 (10)	79.94 (9)	79.94 (7)	80.08 (7)
Avg. Cl4—Zr1—Cl2	79.8 [2]	79.8 [1]	79.9 [9]	79.94 [7]	80.06 [7]

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

structural parameters (Table 1) indicate that there is no phase transformation in this domain of temperature. A linear increase of the unit-cell parameters and volume are observed when moving from 100 to 300 K. In the chain (Fig. 1), the effect of temperature is primarily observed on the Zr1···Zr1ⁱⁱ and Zr1—Cl(bri1,2) (bri denotes bridging) distances, while the Zr1—Cl(ter) (ter is terminal) distances (Table 3) and the angles in the ZrCl₆ octahedron remain almost unchanged (Table 4).

When moving from 100 to 300 K, the Zr1···Zr1ⁱⁱ and the Zr1—Cl(bri1, 2) distances increase by ~0.015 and ~0.006 Å, respectively. The increase of the Zr1···Zr1ⁱⁱ separation is accompanied by a slight decrease of the average Cl4—Zr—Cl2ⁱⁱ angle (*i.e.* 80.06 [7]° at 100 K and 79.8 [2]° at 300 K). The shortest inter-chain distance increases with temperature [*i.e.* Cl1···Cl3* = 3.630 (3) Å at 100 K and 3.687 (9) Å at 300 K], which results in weaker van der Waals interactions at elevated temperatures.

The reaction of Zr metal with excess Cl₂ in a sealed tube leads to ZrCl₄. The space group and structural parameters determined here differ from those of the ZrCl₄ sample prepared previously from ZrO₂ and Cl₂ + CCl₄. The synthetic methods and thermal treatments used might be the origin of the structural differences. In the temperature range 100–

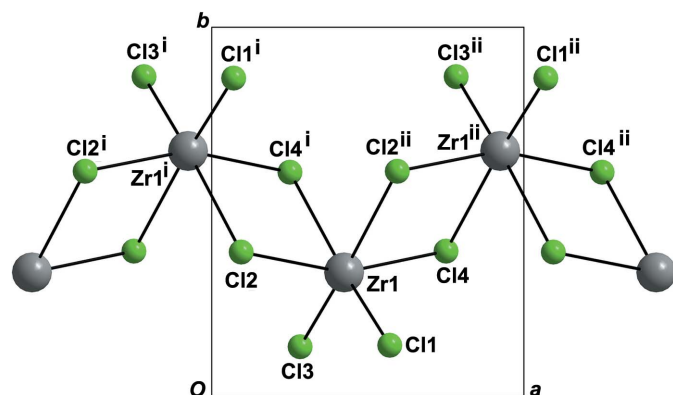


Figure 1
Representation of a fraction of the chain in ZrCl₄ at 300 K. Color key: Zr atoms are grey and Cl are green. The view is along the *c* axis. The distances (Å) are: Zr1—Cl1 = 2.313 (6), Zr1—Cl2 = Zr1—Cl4 = 2.504 (6), Zr1—Cl3 = 2.310 (6), Zr1—Cl2ⁱⁱ = 2.664 (5), Zr1—Cl4ⁱ = 2.670 (5), and Zr1···Zr1ⁱⁱ = 3.968 (5). [Symmetry codes: (i) $x - \frac{1}{2}, -y + 1, z$; (ii) $x + \frac{1}{2}, -y + 1, z$.]

Table 5
Selected bond lengths (Å) in MCl₄, where M = Zr (present work), Hf (Niewa & Jacobs, 1995), and Tc (Elder & Penfold, 1966).

	ZrCl ₄	HfCl ₄	TcCl ₄
M···M1	3.968	3.921	3.62
Avg. M—Cl(bri1)	2.667	2.626	2.492
Avg. M—Cl(bri2)	2.504	2.477	2.382
Avg. M—Cl(ter)	2.312	2.298	2.242
Cl···Cl	3.687	3.743	3.56

300 K, minor changes were observed in the ZrCl₄ structure, *i.e.* elongation of distances (~0.5%) and an increase of the unit-cell volume (~1%) with temperature occurred, while the values of angles in the ZrCl₆ octahedron remained almost unchanged. Zirconium tetrachloride crystallizes with a structure related to TcCl₄, HfCl₄, and PtCl₄ (Table 5). We note that PtCl₄ has not been studied by SCXRD previously (Pilbrow, 1972). Due to the catalytic properties of PtCl₄, determination of its structure by SCXRD is of importance (Michalkiewicz & Kosowski, 2007). It will also provide a better understanding of the structural trends in tetrachlorides of transition metals.

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Computing details

For all structures, data collection: BIS (Bruker, 2016); cell refinement: *APEX3* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2015); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *shelXle* (Hübschle *et al.*, 2011); software used to prepare material for publication: *APEX3* (Bruker, 2016).

Zirconium tetrachloride (SMB_ZrCl4_b_100K)

Crystal data

ZrCl₄

$M_r = 233.02$

Orthorhombic, *Pca*2₁

$a = 6.2199$ (9) Å

$b = 7.3301$ (10) Å

$c = 11.9153$ (16) Å

$V = 543.25$ (13) Å³

$Z = 4$

$F(000) = 432$

$D_x = 2.849$ Mg m⁻³

Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 2790 reflections

$\theta = 2.8\text{--}27.9^\circ$

$\mu = 3.82$ mm⁻¹

$T = 100$ K

Rectangular box, translucent colourless

0.09 × 0.08 × 0.06 mm

Data collection

Bruker D8 QUEST
diffractometer

Radiation source: sealed tube, Siemens
KFFMo2K-90

Curved graphite monochromator

Detector resolution: 8.3333 pixels mm⁻¹

φ and ω scans

Absorption correction: numerical
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.63$, $T_{\max} = 0.81$

5240 measured reflections

924 independent reflections

877 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 24.7^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -7 \rightarrow 7$

$k = -8 \rightarrow 8$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.084$

$S = 1.07$

924 reflections

46 parameters

1 restraint

Primary atom site location: heavy-atom method

Secondary atom site location: difference Fourier
map

$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 2.08$ e Å⁻³

$\Delta\rho_{\min} = -0.53$ e Å⁻³

Absolute structure: Flack x determined using
394 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: -0.05 (15)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Data collections were carried out on a Bruker APEXII system equipped with graphite-monochromated Mo $K\alpha$ radiation (0.71073 Å). A nitrogen-flow Oxford Cryostream-700 was used to control the temperature. Data collections were carried out in the order 100, 150, 200, 250, and 300 K on the same crystal. Data reduction and cell refinement were performed using *SAINTE* and the *APEX3* suite (Bruker, 2016). The structure was solved with *SHELXT* (Sheldrick, 2015a) and an absorption correction was performed with *SADABS* (Sheldrick, 1999). Structure refinements against F^2 were carried out using the *SHELXL* refinement package in *APEX3* (Bruker, 2016). The apparent space group for the structure at all five temperatures was suggested to be orthorhombic $Pca2_1$, by *XPREP*, which differs from that previously described (*i.e.* monoclinic, $P2/c$ (Krebs, 1970)). The refinement yielded R factors varying from 0.0345 at 100 K to 0.0534 at 300 K.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zr1	0.42265 (13)	0.33389 (11)	0.49994 (14)	0.0170 (3)
Cl1	0.5727 (4)	0.1350 (3)	0.6288 (2)	0.0221 (6)
Cl2	0.0920 (4)	0.3893 (3)	0.61382 (19)	0.0189 (6)
Cl3	0.2781 (4)	0.1303 (3)	0.3723 (2)	0.0226 (6)
Cl4	0.7506 (4)	0.3924 (3)	0.38424 (18)	0.0194 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.0132 (4)	0.0184 (5)	0.0193 (5)	0.0001 (4)	0.0003 (4)	0.0003 (6)
Cl1	0.0211 (13)	0.0236 (13)	0.0217 (13)	0.0026 (10)	-0.0024 (10)	0.0043 (10)
Cl2	0.0150 (12)	0.0217 (12)	0.0200 (14)	0.0014 (9)	0.0012 (9)	0.0022 (10)
Cl3	0.0208 (12)	0.0238 (12)	0.0231 (14)	-0.0017 (10)	-0.0020 (12)	-0.0022 (10)
Cl4	0.0153 (11)	0.0219 (12)	0.0211 (14)	-0.0019 (10)	0.0017 (11)	-0.0009 (10)

Geometric parameters (Å, °)

Zr1—Cl3	2.313 (3)	Zr1—Cl2 ⁱ	2.659 (3)
Zr1—Cl1	2.314 (3)	Zr1—Cl4 ⁱⁱ	2.659 (2)
Zr1—Cl2	2.497 (3)	Cl2—Zr1 ⁱⁱ	2.659 (3)
Zr1—Cl4	2.499 (2)	Cl4—Zr1 ⁱ	2.659 (2)
Cl3—Zr1—Cl1	100.75 (9)	Cl4—Zr1—Cl2 ⁱ	80.05 (7)
Cl3—Zr1—Cl2	98.17 (9)	Cl3—Zr1—Cl4 ⁱⁱ	89.40 (9)
Cl1—Zr1—Cl2	94.25 (10)	Cl1—Zr1—Cl4 ⁱⁱ	169.03 (11)
Cl3—Zr1—Cl4	93.74 (10)	Cl2—Zr1—Cl4 ⁱⁱ	80.08 (7)
Cl1—Zr1—Cl4	98.34 (9)	Cl4—Zr1—Cl4 ⁱⁱ	85.01 (7)
Cl2—Zr1—Cl4	160.75 (9)	Cl2 ⁱ —Zr1—Cl4 ⁱⁱ	81.26 (7)

Cl3—Zr1—Cl2 ⁱ	169.16 (11)	Zr1—Cl2—Zr1 ⁱⁱ	99.96 (9)
Cl1—Zr1—Cl2 ⁱ	89.00 (10)	Zr1—Cl4—Zr1 ⁱ	99.90 (9)
Cl2—Zr1—Cl2 ⁱ	85.69 (8)		

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

Zirconium tetrachloride (SMB_ZrCl4a_a_150K)

Crystal data

ZrCl₄

$M_r = 233.02$

Orthorhombic, $Pca2_1$

$a = 6.2311$ (8) Å

$b = 7.3497$ (10) Å

$c = 11.9462$ (15) Å

$V = 547.10$ (12) Å³

$Z = 4$

$F(000) = 432$

$D_x = 2.829$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2581 reflections

$\theta = 2.8$ – 27.9°

$\mu = 3.79$ mm⁻¹

$T = 150$ K

Rectangular plate, translucent colourless

$0.09 \times 0.08 \times 0.06$ mm

Data collection

Bruker D8 QUEST
diffractometer

Radiation source: sealed tube, Siemens
KFFMo2K-90

Curved graphite monochromator

Detector resolution: 8.3333 pixels mm⁻¹

φ and ω scans

Absorption correction: numerical
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.64, T_{\max} = 0.78$

5124 measured reflections

906 independent reflections

853 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.051$

$\theta_{\max} = 24.7^\circ, \theta_{\min} = 6.5^\circ$

$h = -7 \rightarrow 7$

$k = -8 \rightarrow 8$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.080$

$S = 1.04$

906 reflections

46 parameters

1 restraint

Primary atom site location: heavy-atom method

Secondary atom site location: difference Fourier
map

$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 2.08$ e Å⁻³

$\Delta\rho_{\min} = -0.52$ e Å⁻³

Absolute structure: Flack x determined using

374 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: -0.03 (14)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component twin.

Data collections were carried out on a Bruker APEXII system equipped with graphite-monochromated Mo $K\alpha$ radiation (0.71073 Å). A nitrogen-flow Oxford Cryostream-700 was used to control the temperature. Data collections were carried out in the order 100, 150, 200, 250, and 300 K on the same crystal. Data reduction and cell refinement were performed using *SAINTE* and the *APEX3* suite (Bruker, 2016). The structure was solved with *SHELXT* (Sheldrick, 2015a) and an absorption correction was performed with *SADABS* (Sheldrick, 1999). Structure refinements against F^2 were carried out using the *SHELXL* refinement package in *APEX3* (Bruker, 2016). The apparent space group for the structure at all five temperatures was suggested to be orthorhombic $Pca2_1$ by *XPREP*, which differs from that previously described (*i.e.* monoclinic, $P2/c$ (Krebs, 1970)). The refinement yielded R factors varying from 0.0345 at 100 K to 0.0534 at 300 K.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zr1	0.42306 (12)	0.33410 (10)	0.50001 (13)	0.0191 (3)
Cl1	0.5726 (4)	0.1359 (3)	0.6287 (2)	0.0265 (6)
Cl2	0.0927 (4)	0.3896 (3)	0.61336 (18)	0.0211 (6)
Cl3	0.2797 (4)	0.1309 (3)	0.3725 (2)	0.0276 (6)
Cl4	0.7507 (4)	0.3926 (3)	0.38452 (18)	0.0229 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.0150 (4)	0.0208 (5)	0.0213 (5)	0.0002 (4)	0.0005 (4)	0.0006 (5)
Cl1	0.0252 (14)	0.0281 (13)	0.0262 (14)	0.0041 (10)	−0.0028 (10)	0.0042 (11)
Cl2	0.0161 (12)	0.0250 (12)	0.0222 (13)	0.0024 (9)	0.0024 (9)	0.0035 (10)
Cl3	0.0273 (12)	0.0279 (12)	0.0277 (14)	−0.0030 (11)	−0.0037 (13)	−0.0040 (10)
Cl4	0.0184 (11)	0.0254 (11)	0.0247 (14)	−0.0022 (10)	0.0018 (11)	−0.0029 (10)

Geometric parameters (Å, °)

Zr1—Cl3	2.313 (3)	Zr1—Cl2 ⁱ	2.660 (3)
Zr1—Cl1	2.314 (3)	Zr1—Cl4 ⁱⁱ	2.663 (2)
Zr1—Cl2	2.497 (2)	Cl2—Zr1 ⁱⁱ	2.660 (3)
Zr1—Cl4	2.501 (2)	Cl4—Zr1 ⁱ	2.663 (2)
Cl3—Zr1—Cl1	100.76 (9)	Cl4—Zr1—Cl2 ⁱ	79.93 (7)
Cl3—Zr1—Cl2	98.31 (9)	Cl3—Zr1—Cl4 ⁱⁱ	89.43 (10)
Cl1—Zr1—Cl2	94.27 (9)	Cl1—Zr1—Cl4 ⁱⁱ	168.97 (10)
Cl3—Zr1—Cl4	93.60 (10)	Cl2—Zr1—Cl4 ⁱⁱ	79.94 (7)
Cl1—Zr1—Cl4	98.39 (9)	Cl4—Zr1—Cl4 ⁱⁱ	85.05 (7)
Cl2—Zr1—Cl4	160.69 (9)	Cl2 ⁱ —Zr1—Cl4 ⁱⁱ	81.27 (7)
Cl3—Zr1—Cl2 ⁱ	169.05 (11)	Zr1—Cl2—Zr1 ⁱⁱ	100.15 (9)
Cl1—Zr1—Cl2 ⁱ	88.99 (9)	Zr1—Cl4—Zr1 ⁱ	99.96 (9)
Cl2—Zr1—Cl2 ⁱ	85.81 (8)		

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

Zirconium tetrachloride (SMB_ZrCl4_b_200K)

Crystal data

ZrCl₄ $M_r = 233.02$ Orthorhombic, *Pca*2₁ $a = 6.2389$ (8) Å $b = 7.3667$ (10) Å $c = 11.9735$ (16) Å $V = 550.30$ (13) Å³ $Z = 4$ $F(000) = 432$ $D_x = 2.813$ Mg m⁻³Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 2383 reflections

 $\theta = 2.8$ – 28.4° $\mu = 3.77$ mm⁻¹ $T = 200$ K

Rectangular box, translucent colourless

0.09 × 0.08 × 0.06 mm

Data collection

Bruker D8 QUEST

diffractometer

Radiation source: sealed tube, Siemens

KFFMo2K-90

Curved graphite monochromator

Detector resolution: 8.3333 pixels mm⁻¹ φ and ω scans

Absorption correction: numerical

(SADABS; Krause *et al.*, 2015) $T_{\min} = 0.64$, $T_{\max} = 0.82$

5292 measured reflections

934 independent reflections

864 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.049$ $\theta_{\max} = 24.7^\circ$, $\theta_{\min} = 3.4^\circ$ $h = -7 \rightarrow 7$ $k = -8 \rightarrow 8$ $l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.038$ $wR(F^2) = 0.095$ $S = 1.11$

934 reflections

46 parameters

1 restraint

Primary atom site location: heavy-atom method

Secondary atom site location: difference Fourier map

 $w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.3988P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 2.11$ e Å⁻³ $\Delta\rho_{\min} = -0.54$ e Å⁻³Absolute structure: Flack x determined using386 quotients [(1+)-(1-)]/[(1+)+(1-)] (Parsons *et al.*, 2013)

Absolute structure parameter: 0.18 (17)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Data collections were carried out on a Bruker APEXII system equipped with graphite-monochromated Mo *K*α radiation (0.71073 Å). A nitrogen-flow Oxford Cryostream-700 was used to control the temperature. Data collections were carried out in the order 100, 150, 200, 250, and 300 K on the same crystal. Data reduction and cell refinement were performed using *SAINTE* and the *APEX3* suite (Bruker, 2016). The structure was solved with *SHELXT* (Sheldrick, 2015a) and an absorption correction was performed with *SADABS* (Sheldrick, 1999). Structure refinements against F^2 were carried out using the *SHELXL* refinement package in *APEX3* (Bruker, 2016). The apparent space group for the structure at all five temperatures was suggested to be orthorhombic *Pca*2₁ by *XPREP*, which differs from that previously described (*i.e.* monoclinic, *P2/c* (Krebs, 1970)). The refinement yielded *R* factors varying from 0.0345 at 100 K to 0.0534 at 300 K.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zr1	0.42327 (15)	0.33461 (12)	0.50006 (16)	0.0244 (3)

Cl1	0.5717 (5)	0.1372 (4)	0.6283 (3)	0.0346 (8)
Cl2	0.0931 (4)	0.3897 (4)	0.6132 (2)	0.0278 (7)
Cl3	0.2805 (5)	0.1316 (4)	0.3725 (3)	0.0356 (7)
Cl4	0.7508 (4)	0.3931 (4)	0.3848 (2)	0.0288 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.0189 (5)	0.0265 (5)	0.0278 (6)	0.0001 (4)	0.0001 (5)	0.0001 (7)
Cl1	0.0329 (17)	0.0368 (17)	0.0340 (17)	0.0042 (12)	-0.0045 (13)	0.0074 (13)
Cl2	0.0217 (14)	0.0330 (15)	0.0287 (16)	0.0017 (11)	0.0019 (11)	0.0050 (12)
Cl3	0.0344 (16)	0.0359 (16)	0.0365 (18)	-0.0042 (13)	-0.0012 (16)	-0.0048 (13)
Cl4	0.0229 (13)	0.0343 (14)	0.0290 (16)	-0.0017 (12)	0.0025 (13)	-0.0036 (12)

Geometric parameters (Å, °)

Zr1—Cl1	2.309 (3)	Zr1—Cl2 ⁱ	2.661 (3)
Zr1—Cl3	2.316 (3)	Zr1—Cl4 ⁱⁱ	2.662 (3)
Zr1—Cl2	2.499 (3)	Cl2—Zr1 ⁱⁱ	2.661 (3)
Zr1—Cl4	2.503 (3)	Cl4—Zr1 ⁱ	2.662 (3)
Cl1—Zr1—Cl3	100.74 (11)	Cl4—Zr1—Cl2 ⁱ	79.87 (9)
Cl1—Zr1—Cl2	94.15 (11)	Cl1—Zr1—Cl4 ⁱⁱ	168.98 (12)
Cl3—Zr1—Cl2	98.37 (11)	Cl3—Zr1—Cl4 ⁱⁱ	89.38 (12)
Cl1—Zr1—Cl4	98.49 (10)	Cl2—Zr1—Cl4 ⁱⁱ	79.94 (9)
Cl3—Zr1—Cl4	93.52 (12)	Cl4—Zr1—Cl4 ⁱⁱ	85.10 (9)
Cl2—Zr1—Cl4	160.72 (10)	Cl2 ⁱ —Zr1—Cl4 ⁱⁱ	81.36 (8)
Cl1—Zr1—Cl2 ⁱ	88.99 (11)	Zr1—Cl2—Zr1 ⁱⁱ	100.16 (11)
Cl3—Zr1—Cl2 ⁱ	169.01 (13)	Zr1—Cl4—Zr1 ⁱ	100.02 (10)
Cl2—Zr1—Cl2 ⁱ	85.88 (9)		

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

Zirconium tetrachloride (SMB_ZrCl4_b_250K)*Crystal data*Cl₄Zr $M_r = 233.02$ Orthorhombic, $Pca2_1$ $a = 6.253 (5) \text{ \AA}$ $b = 7.383 (6) \text{ \AA}$ $c = 12.017 (9) \text{ \AA}$ $V = 554.8 (7) \text{ \AA}^3$ $Z = 4$ $F(000) = 432$ $D_x = 2.790 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1861 reflections

 $\theta = 2.8\text{--}25.8^\circ$ $\mu = 3.74 \text{ mm}^{-1}$ $T = 250 \text{ K}$

Rectangular plate, translucent colourless

 $0.09 \times 0.08 \times 0.06 \text{ mm}$ *Data collection*

Bruker D8 QUEST

diffractometer

Radiation source: sealed tube, Siemens

KFFMo2K-90

Curved graphite monochromator

Detector resolution: $8.3333 \text{ pixels mm}^{-1}$ φ and ω scans

Absorption correction: numerical
(SADABS; Krause *et al.*, 2015)
 $T_{\min} = 0.63$, $T_{\max} = 0.81$
5285 measured reflections
934 independent reflections
815 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.063$
 $\theta_{\text{max}} = 24.7^\circ$, $\theta_{\text{min}} = 4.3^\circ$
 $h = -7 \rightarrow 7$
 $k = -8 \rightarrow 8$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.096$
 $S = 1.05$
934 reflections
46 parameters
1 restraint
Primary atom site location: heavy-atom method

Secondary atom site location: difference Fourier map
 $w = 1/[\sigma^2(F_o^2) + (0.0566P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 2.13 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.48 \text{ e } \text{\AA}^{-3}$
Absolute structure: Flack x determined using 351 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.01 (15)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Data collections were carried out on a Bruker APEXII system equipped with graphite-monochromated Mo $K\alpha$ radiation (0.71073 Å). A nitrogen-flow Oxford Cryostream-700 was used to control the temperature. Data collections were carried out in the order 100, 150, 200, 250, and 300 K on the same crystal. Data reduction and cell refinement were performed using *SAINTE* and the *APEX3* suite (Bruker, 2016). The structure was solved with *SHELXT* (Sheldrick, 2015a) and an absorption correction was performed with *SADABS* (Sheldrick, 1999). Structure refinements against F^2 were carried out using the *SHELXL* refinement package in *APEX3* (Bruker, 2016). The apparent space group for the structure at all five temperatures was suggested to be orthorhombic Pca_2 , by *XPREP*, which differs from that previously described (*i.e.* monoclinic, $P2/c$ (Krebs, 1970)). The refinement yielded R factors varying from 0.0345 at 100 K to 0.0534 at 300 K.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zr1	0.42359 (16)	0.33495 (13)	0.50035 (17)	0.0260 (4)
Cl2	0.0938 (5)	0.3902 (4)	0.3876 (2)	0.0303 (8)
Cl3	0.2820 (5)	0.1329 (4)	0.6274 (3)	0.0408 (9)
Cl1	0.5717 (6)	0.1375 (5)	0.3721 (3)	0.0395 (9)
Cl4	0.7504 (5)	0.3927 (4)	0.6150 (2)	0.0321 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.0210 (5)	0.0289 (6)	0.0282 (6)	-0.0003 (5)	-0.0002 (6)	0.0007 (7)
Cl2	0.0239 (16)	0.0373 (17)	0.0296 (18)	0.0021 (13)	-0.0020 (13)	-0.0062 (14)
Cl3	0.0396 (19)	0.0415 (18)	0.041 (2)	-0.0060 (16)	0.0054 (19)	0.0064 (15)
Cl1	0.041 (2)	0.0397 (19)	0.038 (2)	0.0059 (15)	0.0033 (15)	-0.0104 (15)
Cl4	0.0263 (15)	0.0374 (16)	0.032 (2)	-0.0036 (14)	-0.0052 (15)	0.0069 (14)

Geometric parameters (Å, °)

Zr1—Cl3	2.311 (4)	Zr1—Cl2 ⁱ	2.662 (4)
Zr1—Cl1	2.315 (4)	Zr1—Cl4 ⁱⁱ	2.667 (3)
Zr1—Cl2	2.501 (4)	Cl2—Zr1 ⁱⁱ	2.662 (4)
Zr1—Cl4	2.501 (4)	Cl4—Zr1 ⁱ	2.667 (3)
Cl3—Zr1—Cl1	100.76 (13)	Cl4—Zr1—Cl2 ⁱ	79.85 (10)
Cl3—Zr1—Cl2	98.46 (13)	Cl3—Zr1—Cl4 ⁱⁱ	89.41 (14)
Cl1—Zr1—Cl2	94.12 (13)	Cl1—Zr1—Cl4 ⁱⁱ	168.86 (14)
Cl3—Zr1—Cl4	93.40 (14)	Cl2—Zr1—Cl4 ⁱⁱ	79.76 (10)
Cl1—Zr1—Cl4	98.47 (12)	Cl4—Zr1—Cl4 ⁱⁱ	85.33 (11)
Cl2—Zr1—Cl4	160.79 (11)	Cl2 ⁱ —Zr1—Cl4 ⁱⁱ	81.41 (11)
Cl3—Zr1—Cl2 ⁱ	168.98 (14)	Zr1—Cl2—Zr1 ⁱⁱ	100.26 (12)
Cl1—Zr1—Cl2 ⁱ	88.92 (14)	Zr1—Cl4—Zr1 ⁱ	100.12 (12)
Cl2—Zr1—Cl2 ⁱ	85.96 (11)		

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

Zirconium tetrachloride (SMB_ZrCl4_b_300K)

Crystal data

ZrCl₄

$M_r = 233.02$

Orthorhombic, $Pca2_1$

$a = 6.262$ (9) Å

$b = 7.402$ (11) Å

$c = 12.039$ (17) Å

$V = 558.0$ (14) Å³

$Z = 4$

$F(000) = 432$

Data collection

Bruker D8 QUEST
diffractometer

Radiation source: sealed tube, Siemens
KFFMo2K-90

Curved graphite monochromator

Detector resolution: 8.3333 pixels mm⁻¹

φ and ω scans

Absorption correction: numerical
(SADABS; Krause *et al.*, 2015)

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.053$

$wR(F^2) = 0.138$

$S = 1.02$

949 reflections

46 parameters

1 restraint

Primary atom site location: heavy-atom method

$D_x = 2.773$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1130 reflections

$\theta = 2.8\text{--}24.5^\circ$

$\mu = 3.71$ mm⁻¹

$T = 300$ K

Rectangular box, translucent colourless

$0.09 \times 0.08 \times 0.06$ mm

$T_{\min} = 0.55, T_{\max} = 0.81$

5334 measured reflections

949 independent reflections

737 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.093$

$\theta_{\max} = 24.7^\circ, \theta_{\min} = 3.4^\circ$

$h = -7 \rightarrow 7$

$k = -8 \rightarrow 8$

$l = -14 \rightarrow 14$

Secondary atom site location: difference Fourier
map

$w = 1/[\sigma^2(F_o^2) + (0.0788P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 2.59$ e Å⁻³

$\Delta\rho_{\min} = -0.70$ e Å⁻³

Absolute structure: Flack x determined using

284 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.0 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Data collections were carried out on a Bruker APEXII system equipped with graphite-monochromated Mo $K\alpha$ radiation (0.71073 Å). A nitrogen-flow Oxford Cryostream-700 was used to control the temperature. Data collections were carried out in the order 100, 150, 200, 250, and 300 K on the same crystal. Data reduction and cell refinement were performed using *SAINT* and the *APEX3* suite (Bruker, 2016). The structure was solved with *SHELXT* (Sheldrick, 2015a) and an absorption correction was performed with *SADABS* (Sheldrick, 1999). Structure refinements against F^2 were carried out using the *SHELXL* refinement package in *APEX3* (Bruker, 2016). The apparent space group for the structure at all five temperatures was suggested to be orthorhombic $Pca2_1$, by *XPREP*, which differs from that previously described (*i.e.* monoclinic, $P2_1/c$ (Krebs, 1970)). The refinement yielded R factors varying from 0.0345 at 100 K to 0.0534 at 300 K.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zr1	0.4239 (2)	0.3354 (2)	0.5000 (3)	0.0356 (5)
Cl1	0.5702 (8)	0.1380 (7)	0.6280 (4)	0.0515 (15)
Cl2	0.0942 (7)	0.3905 (7)	0.6127 (4)	0.0391 (12)
Cl3	0.2829 (9)	0.1339 (7)	0.3731 (5)	0.0536 (14)
Cl4	0.7504 (7)	0.3930 (6)	0.3853 (4)	0.0407 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.0273 (8)	0.0381 (9)	0.0413 (10)	0.0009 (8)	0.0001 (10)	0.0002 (12)
Cl1	0.047 (3)	0.054 (3)	0.053 (4)	0.006 (3)	−0.005 (3)	0.011 (3)
Cl2	0.032 (3)	0.046 (3)	0.040 (3)	0.004 (2)	0.004 (2)	0.007 (2)
Cl3	0.054 (3)	0.050 (3)	0.056 (3)	−0.006 (3)	−0.004 (3)	−0.009 (3)
Cl4	0.033 (2)	0.046 (3)	0.043 (3)	−0.004 (2)	0.007 (2)	−0.007 (2)

Geometric parameters (Å, °)

Zr1—Cl3	2.310 (6)	Zr1—Cl2 ⁱ	2.664 (5)
Zr1—Cl1	2.313 (6)	Zr1—Cl4 ⁱⁱ	2.670 (5)
Zr1—Cl4	2.504 (6)	Cl2—Zr1 ⁱⁱ	2.664 (5)
Zr1—Cl2	2.504 (6)	Cl4—Zr1 ⁱ	2.670 (5)
Cl3—Zr1—Cl1	100.6 (2)	Cl2—Zr1—Cl2 ⁱ	85.99 (17)
Cl3—Zr1—Cl4	93.3 (2)	Cl3—Zr1—Cl4 ⁱⁱ	89.4 (2)
Cl1—Zr1—Cl4	98.73 (19)	Cl1—Zr1—Cl4 ⁱⁱ	169.0 (2)
Cl3—Zr1—Cl2	98.5 (2)	Cl4—Zr1—Cl4 ⁱⁱ	85.34 (17)
Cl1—Zr1—Cl2	93.9 (2)	Cl2—Zr1—Cl4 ⁱⁱ	79.76 (16)
Cl4—Zr1—Cl2	160.82 (17)	Cl2 ⁱ —Zr1—Cl4 ⁱⁱ	81.54 (17)
Cl3—Zr1—Cl2 ⁱ	169.0 (2)	Zr1—Cl2—Zr1 ⁱⁱ	100.26 (19)
Cl1—Zr1—Cl2 ⁱ	89.0 (2)	Zr1—Cl4—Zr1 ⁱ	100.08 (19)
Cl4—Zr1—Cl2 ⁱ	79.89 (16)		

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

Lattice parameters of ZrCl₄ as measured at the given temperatures

	300 K	250 K	200 K	150 K	100 K
a (Å)	6.262 (9)	6.253 (5)	6.2389 (8)	6.2311 (8)	6.2199 (9)
b (Å)	7.402 (11)	7.383 (6)	7.3667 (10)	7.3497 (10)	7.3301 (10)
c (Å)	12.039 (17)	12.017 (9)	11.9735 (16)	11.9462 (15)	11.9153 (16)
$\alpha = \beta = \gamma$ (°)	90	90	90	90	90
V (Å ³)	558.0 (14)	554.8 (7)	550.30 (13)	547.10 (12)	543.25 (13)
Z	4	4	4	4	4
R factor	5.33%	3.82%	3.76%	3.34%	3.45%