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Structure of Aquatetrafluorozirconium(IV)

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Abstract

$[ZrF_4(H_2O)]$, $M_r = 185 \cdot 24$, crystallizes in the tetragonal space group $I\bar{4}2d$ with $a = 7 \cdot 724\,(2)$, $c = 11 \cdot 678\,(4)$ Å, $Z = 8$, $U = 696 \cdot 7$ Å^3, $D_m = 3 \cdot 500$, $D_c = 3 \cdot 533$ Mg m^{-3}, μ(Mo $K\alpha$) = $3 \cdot 068$ mm^{-1}. Final $R = 0 \cdot 026$ for 414 observed reflexions. The basic structural unit is $[ZrF_6(H_2O)_2]$ with dodecahedral coordination. The Zr—F distances are 2·058 (2), 2·100 (3) and 2·170 (2) Å and Zr—O(W) is 2·132 (1) Å. Each Zr polyhedron shares six corners with six adjacent polyhedra forming an infinite three-dimensional network.

Introduction

A mono- and a trihydrate of zirconium tetrafluoride were reported by Chauvenet (1920). In addition to chemical analysis, X-ray powder diffraction (D'Eye, Burden & Harper, 1956), IR (Kolditz & Feltz, 1961) and NMR (proton and fluorine magnetic resonance) (Maričić, Strohal & Veksli, 1963) techniques were used in characterizing these zirconium fluorides. The ZrF_4/H_2O system has been reinvestigated by Waters (1960). Unit-cell parameters of $ZrF_4.H_2O$ given by Waters (1960) are in good agreement with our data.

Experimental

The space group was determined from Weissenberg photographs recorded with Cu $K\alpha$ radiation. The diffraction symmetry and extinctions indicated the space group $I\bar{4}2d$ and this was confirmed during structure refinement. The intensities were collected with a crystal of dimensions 0·020 × 0·030 × 0·04 mm on a Philips PW 1100 computer-controlled four-circle diffractometer in the ω-scan mode [scan width = 1·60°(θ), scan speed = 0·040°(θ) s^{-1}] with graphite-monochromated Mo $K\alpha$ radiation. 414 independent reflexions [$I > 2\sigma(I)$] in the range $3 < \theta < 34°$ were recorded and used in the calculations. Three standard reflexions were measured every 2 h. The data were corrected for background, Lorentz and polarization effects.

Structure determination and refinement

The Patterson map was solved in $I\bar{4}2d$, which showed that the Zr atom is positioned on the twofold axis at site 8(d). A Fourier synthesis based on the coordinates of the Zr atom revealed the two F atoms in general positions and a water molecule on the other twofold axis, site 8(c). The structure was refined by full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$. Weights were assigned as $w = w_1.w_2$ where $w_1 = 1$ for $|F_o| \le 35$ and $35/|F_o|$ for $|F_o| > 35$; $w_2 = 1$ for $\sin\theta \ge 0 \cdot 40$ and $\sin\theta/0 \cdot 40$ for $\sin\theta < 0 \cdot 40$. A scale factor, atomic coordinates, and anisotropic thermal parameters (29 variables in all) were refined. Anisotropic thermal parameters are in the usual range: the maximum value is U_{33} for F(1) [0·033 (1) Å^2]. The final $R = 0 \cdot 026$ and $R_w = 0 \cdot 030$ for 414 reflexions with $I > 2\sigma(I)$.

The scattering factors given by Cromer & Mann (1968) were used. An anomalous-dispersion correction was included for Zr (Cromer & Liberman, 1970).

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Table 1. *Atomic coordinates* ($\times 10^5$) *and equivalent isotropic thermal parameters* ($\times 10^2$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2)
Zr	10800 (5)	25000	12500	0·52 (6)
O(W)	0	0	15466 (28)	0·65 (14)
F(1)	29533 (41)	11750 (38)	22149 (30)	2·20 (24)
F(2)	22519 (31)	42639 (31)	24711 (22)	1·29 (18)

Calculations were carried out on a Univac 1110 computer at the University Computing Centre in Zagreb with the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.*

Description and discussion of the structure

Zirconium coordination

The Zr atom is coordinated by six F atoms [F(1), F(2), F(1^{i}), F(2^{i}), F(2^{ii}), F(2^{iii})] and two water molecules [O(W), O(W^{iv})] forming $ZrF_6(H_2O)_2$ structural units. The polyhedron around the Zr atom is a dodecahedron (Fig. 1) which shares corners with six adjacent polyhedra. The Zr—F distances are 2·058 (2), 2·100 (3) and 2·170 (2) Å and Zr—O(W) is 2·132 (1) Å (Table 2). An analogous structural unit of [$HfF_6(H_2O)_2$] is found in the structure of *catena*-diaqua-di-μ-fluoro-difluorohafnium(IV) monohydrate (Hall, Rickard & Waters, 1971), one of the dimorphs of $HfF_4.3H_2O$. Here however the overall crystal structure is different.

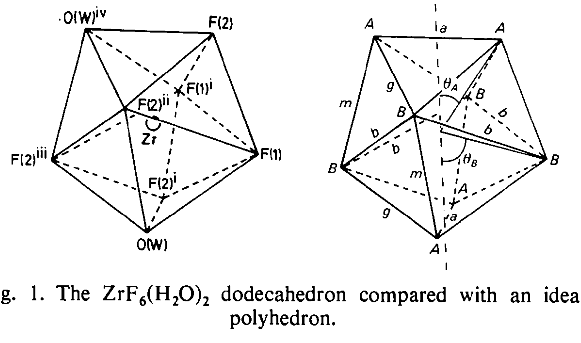

Fig. 1. The $ZrF_6(H_2O)_2$ dodecahedron compared with an ideal polyhedron.

Table 2. *Bond distances* (Å) *and angles* (°) *within the* Zr *polyhedron*

Zr—O	2·132 (1)	F(1)···F(2^{ii})	3·119 (4)
Zr—F(1)	2·100 (3)	F(2)···F(2^{ii})	2·589 (3)
Zr—F(2)	2·170 (2)	F(2^{ii})···F(2^{iii})	3·011 (4)
Zr—F(2^{ii})	2·058 (2)	O(W)···F(1)	2·576 (3)
F(1)···F(1^{i})	3·044 (5)	O(W)···F(2^{i})	2·547 (3)
F(1)···F(2)	2·465 (4)	O(W)···F(2^{ii})	2·479 (3)
F(1)···F(2^{i})	2·632 (4)	O(W)···F(2^{iii})	2·595 (3)
F(1)—Zr—F(2)	70·5 (1)	F(2^{ii})—Zr—F(2^{iii})	94·0 (1)
F(1)—Zr—F(1^{i})	92·9 (1)	O(W)—Zr—F(1)	75·0 (1)
F(1)—Zr—F(2^{ii})	97·2 (1)	O(W)—Zr—F(2^{ii})	72·5 (1)
F(2)—Zr—F(1^{i})	76·1 (1)	O(W)—Zr—F(2^{iii})	76·5 (1)
F(2)—Zr—F(2^{ii})	75·5 (1)	O(W)—Zr—F(2^{i})	72·6 (1)

Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{4} - z$; (ii) $-\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z$: (iii) $-\frac{1}{2} + y, x, -\frac{1}{4} + z$; (iv) $-x, \frac{1}{2} + y, \frac{1}{4} - z$.

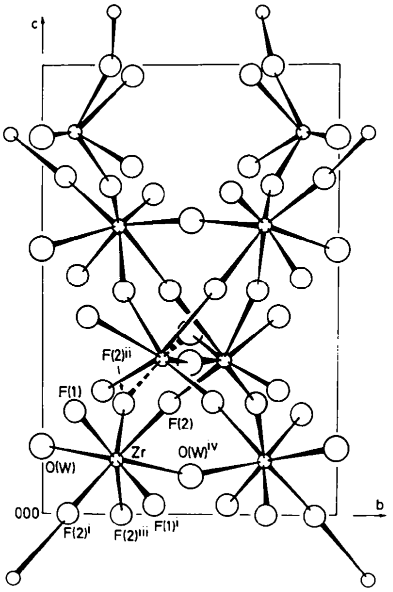

Fig. 2. View of the crystal structure along **a**. Each $ZrF_6(H_2O)_2$ dodecahedron shares six corners with six adjacent polyhedra forming an infinite three-dimensional network. The atoms connected to the Zr atom with dashed lines are translated +1 in the **x** direction.

Table 3. *Geometrical parameters for the real dodecahedron compared with the hard-sphere model and most favourable polyhedron* (*Hoard & Silverton,* 1963) (*see Fig.* 1)

The unit of length is the mean Zr—ligand distance.

[$ZrF_6(H_2O)_2$]	Hard-sphere model	Most favourable polyhedron
$a = 1·18$	$a = m = g = 1·199$	$a = m = 1·17$
$m = 1·17$		
$g = 1·23$		$g = 1·24$
$b = 1·48$	$b = 1·499$	$b = 1·49$
$\theta_A = 36·3°$	$\theta_A = 36·9°$	$\theta_A = 35·2°$
$\theta_B = 62·9°$	$\theta_B = 69·5°$	$\theta_B = 73·5°$
$M - A/M - B = 1·03$	$M - A/M - B = 1·00$	$M - A/M - B = 1·03$

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36140 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

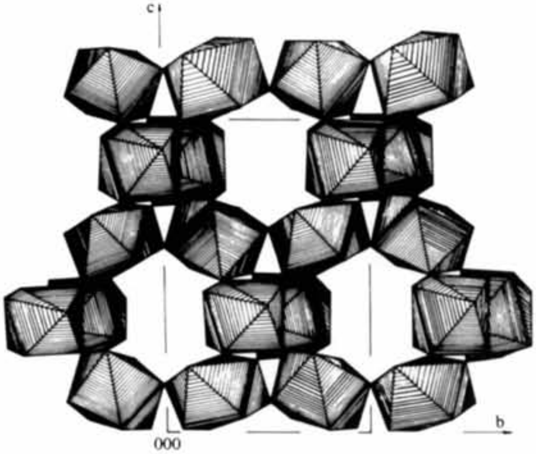

Fig. 3. The three-dimensional network of polyhedra showing the channels between the F(1) corners of the polyhedra parallel to **a** at **b** $\simeq 0$, **c** $\simeq \frac{3}{8}$; **b** $\simeq \frac{1}{2}$, **c** $\simeq \frac{7}{8}$ and parallel to **b** at **a** $\simeq 0$, **c** $\simeq \frac{5}{8}$; **a** $\simeq \frac{1}{2}$; **c** $\simeq \frac{1}{8}$.

Geometrical parameters of the $ZrF_6(H_2O)$ dodecahedron are compared with the hard-sphere model (Hoard & Silverton, 1963; Kepert, 1965, 1978) in Table 3. The shape of the dodecahedron is defined by the angles θ_A, θ_B made by the bonds $M-A$, $M-B$ with the unique axis and the ratio of the bond lengths. The occurrence of an infinite network of polyhedra instead of discrete polyhedra, and dissimilar ligands [F, O(W)] together with the ligand repulsions cause the departure of the dodecahedron from ideality. A more stable structure can often be obtained by distortion of the structure based on the hard-sphere model and this is observed here.

Molecular packing

The structure consists of a three-dimensional network of $ZrF_6(H_2O)_2$ polyhedra sharing six corners (Fig. 2) through atoms O(W), O($W^{\rm iv}$), and F(2), F($2^{\rm i}$), F($2^{\rm ii}$), F($2^{\rm iii}$). F(1) and F($1^{\rm i}$) are disposed at free corners of the polyhedron. Fig. 3 shows the three-dimensional network of polyhedra. The water molecule is surrounded by eight F atoms arranged at the corners of a cube at distances O(W)$\cdots$F 2·479 (3), 2·547 (3), 2·576 (3) and 2·595 (3) Å. A trifurcated O(W)–H$\cdots$F hydrogen bond might be expected.

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Neutron Powder Diffraction Investigation of Pure and Deuterated Palladium Phosphide Pd_6P

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Abstract

A structure proposal for Pd_6P has been refined by the Rietveld method from neutron powder diffraction profile data to a weighted profile R_{wp} value of 0·055, based on 1000 measured points in the profile. The space group is $P2_1/c$ with a = 5·6740 (4), b = 9·4409 (6), c = 8·2100 (6) Å, β = 110·414 (4)°, U =

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