mental data. The electrostatic valence balance reported in Table 4 was computed according to the method of Brown & Shannon (1973); as can be seen, the contribution of H(2) was wholly assigned to the hydrogen donor O(10).

In addition to some local programs, the following for the CII 10070 computer were used: *MULTAN* (Germain, Main & Woolfson, 1971), *ORFLS* (Busing, Martin & Levy, 1962), and *BONDLA* (from the XRAY system, 1972).

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Refinement of the Crystal Structure of Di-μ-fluoro-hexafluorohexaaquadizirconium(IV), Zr$_2$F$_8$(H$_2$O)$_6$

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Crystals of $ZrF_4.3H_2O$ are triclinic, space group $P\bar{1}$ with $a = 5\cdot948$, $b = 6\cdot964$, $c = 7\cdot572$ Å, $\alpha = 90\cdot55$, $\beta = 105\cdot06$, $\gamma = 118\cdot72°$, $Z = 2$. The structure was refined to $R = 0\cdot034$. In the crystal F-bridged binuclear units $Zr_2F_8(H_2O)_6$ exist, each Zr atom being in dodecahedral eight coordination. The Zr–F bonds range from $1\cdot996$ (4) to $2\cdot214$ (3) Å. Zr–O(W) distances are $2\cdot263$ (6), $2\cdot264$ (5) and $2\cdot323$ (5) Å. The packing is dominated by six crystallographically independent hydrogen bonds O–H$\cdots$F and O–H$\cdots$O acting between three water molecules and four F atoms.

Introduction

The existence of a mono- and a trihydrate of zirconium tetrafluoride was reported by Chauvenet (1920). They have been identified from X-ray powder diffraction patterns and chemical studies (D'Eye, Burden & Harper, 1956). The ZrF_4/H_2O system has been reinvestigated by Waters (1960). Cell parameters of

ZrF$_4$.3H$_2$O given by Waters (1960, 1964) are in good agreement with the present data. The structure established on the basis of two-dimensional X-ray data (Waters, 1964) is also in agreement with the present structure, except that it lacked atomic coordinates and any information about hydrogen bonds. Structural studies of transition-metal fluorides have occupied our attention for some years (Kojić-Prodić, Ščavničar & Matković, 1971; Kojić-Prodić, Matković & Ščavničar, 1971; Kojić-Prodić, Ščavničar, Liminga & Šljukić, 1972; Ružić-Toroš, Kojić-Prodić & Šljukić, 1976; Ružić-Toroš, Kojić-Prodić, Gabela & Šljukić, 1977). In particular, the stereochemistry of Zr is of interest and we considered it worth while to complete the crystal structure investigation of ZrF$_4$.3H$_2$O.

Experimental

Crystallographic and physical data are listed in Table 1. The density was measured at 20°C pycnometrically with decalin.

Intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer by the ω-scan mode (scan width = 1·2° θ, scan speed = 0·04° θ s^{-1}) with graphite-monochromated Mo $K\alpha$ radiation. 1483 independent observed reflexions in the range 2 < θ < 30° were recorded and only these were used in the calculations. Three standard reflexions were measured every 2 h and showed no significant variation.

The data were corrected for background, Lorentz and polarization effects, and for monochromator polarization.

Structure determination and refinement

The Patterson map was successfully solved in $P\bar{1}$, implying a binuclear unit formed across a centre of symmetry. A Fourier synthesis based on the coordinates of the Zr atoms revealed the positions of four F and three O atoms. Full-matrix least squares, minimizing $\Sigma w ||F_o| - |F_c||^2$ with $w = 1/\sigma_{Fo}^2$, was used for

Table 1. *Crystallographic and physical data*

Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digit.

ZrF$_4$.3H$_2$O   FW 221·26
Space group $P\bar{1}$ U = 262·26 Å^3
a = 5·948 (2) Å Z = 2
b = 6·964 (2) D_m = 2·792 g cm^{-3}
c = 7·572 (3) D_c = 2·801
α = 90·55 (1)° μ (Mo $K\alpha$) = 20·9 cm^{-1}
β = 105·06 (1)
γ = 118·72 (3)

Table 2. *Final atomic (×10^4) parameters for non-hydrogen atoms*

	x	y	z
Zr	2640 (1)	1482 (1)	2167 (1)
F(1)	2724 (7)	4103 (6)	1073 (5)
F(2)	−1651 (6)	50 (6)	566 (4)
F(3)	642 (7)	−959 (6)	3479 (5)
F(4)	5480 (6)	2956 (5)	4669 (4)
O(W1)	821 (7)	2926 (6)	3785 (5)
O(W2)	4516 (9)	−704 (7)	2436 (6)
O(W3)	6549 (8)	3272 (7)	1456 (6)

Table 3. *Positional (×10^3) and isotropic thermal parameters (Å^2 × 10^2) for hydrogen atoms*

	x	y	z	U
H(W1)1	27	233	472	2·5
H(W1)2	210	433	431	1·4
H(W2)1	583	−50	183	4·3
H(W2)2	447	−183	335	6·1
H(W3)1	693	450	83	2·8
H(W3)2	793	333	194	2·9

refinement. Isotropic refinement led to R = 0·06. Anisotropic refinement (R = 0·037) and a subsequent difference synthesis located the H atoms. In the final cycles one scale factor, the atomic coordinates and anisotropic thermal parameters (73 parameters) were varied. H atoms were not refined. The final R (= $\Sigma ||F_o| - |F_c||/\Sigma |F_o|$) was 0·034 and R_w {= [$\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2$]$^{1/2}$} was 0·051.

Scattering factors given by Cromer & Mann (1968) and (for H) by Stewart, Davidson & Simpson (1965) were used. An anomalous dispersion correction was included for Zr (Cromer & Liberman, 1970).

The calculations were carried out on the Univac 1110 computer at the University Computing Center in Zagreb with the XRAY 72/73 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1973).

Positional and thermal parameters are listed in Tables 2 and 3.*

Description and discussion of the structure

Coordination around the zirconium atom

The Zr atom is coordinated by four F atoms [F(1),F(2),F(3),F(4)] and three water molecules [O(W1),O(W2),O(W3)]. The eightfold coordination is

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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 32803 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

completed by a symmetry-related F(2^i) (Fig. 1). F(2) and F(2^i) act as a bridge between two Zr atoms. The Zr–F bonds range from 1·996 (4) to 2·214 (3) Å (Table 4). The Zr–O(*W*) distances are 2·263 (6), 2·264 (5) and 2·323 (5) Å. The intra-ionic F···F distances range from 2·367 (4) to 3·118 (5) Å. The distance between F(2) and F(2^i), 2·367 (4) Å, may be compared with 2·357 (4) Å in K$_2$NbF$_7$ (Brown & Walker, 1966). The Zr···Zr distance is 3·630 (5) Å.

The polyhedron around the Zr atom is a dodecahedron (Fig. 2) which shares one edge with another Zr atom belonging to the same dimer unit. Geometrical parameters of the Zr$_2$F$_8$(H$_2$O)$_6$ dodecahedron are compared with the hard-sphere model (Hoard & Silverton, 1963; Kepert, 1965) in Table 5. The shape of
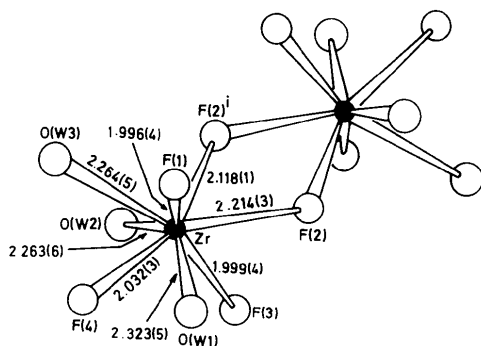
the dodecahedron is defined by the angles θ_A, θ_B which the bonds M–A, M–B make with the unique axis and the ratio of bond lengths. The presence of a common edge between two dodecahedra and also different ligands [F,O(W)] influence the departure of the dodecahedra from ideality. A more stable structure can
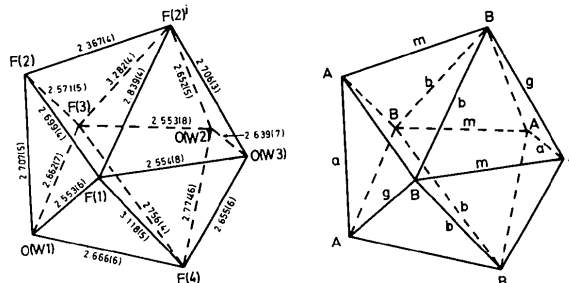

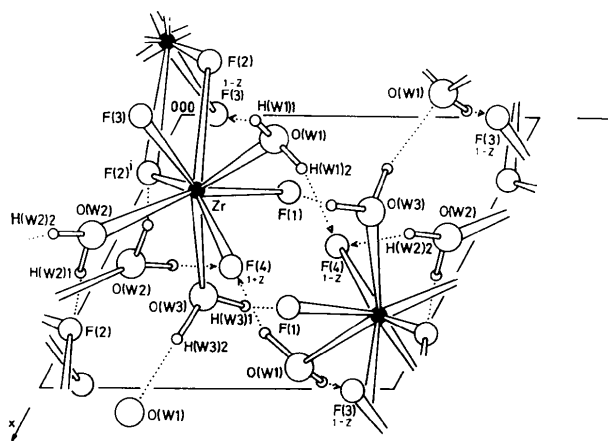Fig. 2. Dodecahedron around the Zr atom compared with an ideal polyhedron.

Fig. 1. The coordination around the Zr atom.

Fig. 3. The packing arrangement, dominated by the hydrogen bonds acting between the fluorine atoms and water molecules.

Table 4. *Interatomic distances (Å) and angles (°) in the Zr polyhedron*

Symmetry operation: (i) (x,y,z) → (−x, −y, −z).

Zr–F(1)	1·996 (4)	F(4)···O(W1)	2·666 (6)
Zr–F(2)	2·214 (3)	F(4)···O(W2)	2·774 (6)
Zr–F(2^i)	2·118 (1)	F(4)···O(W3)	2·655 (6)
Zr–F(3)	1·999 (4)	O(W2)···O(W3)	2·639 (7)
Zr–F(4)	2·032 (3)	F(1)–Zr–F(2)	79·6 (1)
Zr–O(W1)	2·323 (5)	F(1)–Zr–F(2^i)	87·2 (1)
Zr–O(W2)	2·263 (6)	F(1)–Zr–F(4)	101·4 (1)
Zr–O(W3)	2·264 (5)	F(1)–Zr–O(W1)	72·0 (2)
F(1)···F(2)	2·699 (4)	F(1)–Zr–O(W3)	73·3 (2)
F(1)···F(2^i)	2·839 (4)	F(2)–Zr–F(2^i)	66·2 (1)
F(1)···F(4)	3·118 (5)	F(2)–Zr–F(3)	75·0 (1)
F(1)···O(W1)	2·553 (6)	F(2)–Zr–O(W1)	73·2 (1)
F(1)···O(W3)	2·554 (8)	F(2^i)–Zr–F(3)	105·7 (1)
F(2)···F(2^i)	2·367 (4)	F(2^i)–Zr–O(W2)	74·4 (1)
F(2)···F(3)	2·571 (5)	F(2^i)–Zr–O(W3)	76·2 (1)
F(2)···O(W1)	2·707 (5)	F(3)–Zr–F(4)	86·2 (1)
F(2^i)···F(3)	3·282 (4)	F(3)–Zr–O(W1)	75·6 (2)
F(2^i)···O(W2)	2·652 (5)	F(3)–Zr–O(W2)	73·3 (2)
F(2^i)···O(W3)	2·706 (3)	F(4)–Zr–O(W1)	75·1 (1)
F(3)···F(4)	2·756 (4)	F(4)–Zr–O(W2)	80·2 (2)
F(3)···O(W1)	2·662 (7)	F(4)–Zr–O(W3)	76·1 (1)
F(3)···O(W2)	2·553 (8)	O(W2)–Zr–O(W3)	71·3 (2)

Table 5. *Geometrical parameters for the real dodecahedron compared with the hard-sphere model and most favourable polyhedron*

The edge lengths are expressed in the mean Zr–ligand bond-distance units.

Zr$_2$F$_8$(H$_2$O)$_6$	Hard-sphere model	Most favourable polyhedron
$a = 1·19$	$a = m = g = 1·199$	$a = m = 1·17$
$m = 1·15$		
$g = 1·21$		$g = 1·24$
$b = 1·47$	$b = 1·499$	$b = 1·49$
$\theta_A = 36·60°$	$\theta_A = 36·9°$	$\theta_A = 35·2°$
$\theta_B = 75·0°$	$\theta_B = 69·5°$	$\theta_B = 73·5°$
M–A/M–$B = 1·09$	M–A/M–$B = 1·00$	M–A/M–$B = 1·03$

Table 6. *Hydrogen-bond distances* (Å) *and angles* (°)

X–H$\cdots Y$	$X\cdots Y$	X–H	H$\cdots Y$	X–H$\cdots Y$	Symmetry operation
O(W1)–H(W1)1$\cdots$F(3)	2·602 (5)	0·88	1·72	173	$x,y,z;\quad -x,-y,1-z$
O(W1)–H(W1)2$\cdots$F(4)	2·640 (4)	0·90	1·74	179	$x,y,z;\quad 1-x,1-y,1-z$
O(W2)–H(W2)1$\cdots$F(2)	2·652 (6)	0·96	1·87	176	$x,y,z;\quad -x,-y,-z$
O(W2)–H(W2)2$\cdots$F(4)	2·708 (6)	1·05	1·70	160	$x,y,z;\quad 1-x,-y,1-z$
O(W3)–H(W3)1$\cdots$F(1)	2·633 (6)	0·94	1·75	155	$x,y,z;\quad 1-x,1-y,-z$
O(W3)–H(W3)2$\cdots$O(W1)	2·809 (7)	0·79	2·05	161	$x,y,z;\quad 1+x,y,z$

often be obtained by a distortion from the structure based on the hard-sphere model and this is observed here.

Molecular packing

The structure is a three-dimensional network of $Zr_2F_8(H_2O)_6$ dimers connected by hydrogen bonds O–H$\cdots$F and O–H$\cdots$O (Fig. 3). All water molecules are coordinated to the Zr atom but they are also involved in hydrogen bonds with four F atoms (Table 6). O(W1) and O(W2) are hydrogen-bonded to F atoms only: O(W1)$\cdots$F(3) 2·602 (5), O(W1)$\cdots$F(4) 2·640 (4), O(W2)$\cdots$F(2) 2·652 (6), O(W2)$\cdots$F(4) 2·708 (6) Å. O(W3) is engaged in O(W3)$\cdots$F(1), 2·633 (6), and O(W3)$\cdots$O(W1), 2·809 (7) Å, hydrogen bonds.

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