

value of the *R* factor seems to arise from the easily disordered perchlorate group, although two sets of independent data were taken and averaged.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55785 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1020]

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Structures of $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$ and $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$

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Abstract

μ -Difluoro-bis[bis(dimethyl sulfoxide)trifluorozirconium], $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$, crystallizes in a monoclinic space group; the structure is built up from isolated $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$ bipolyhedra formed by edge sharing of $[\text{ZrF}_5(\text{dmsO})_2]$ pentagonal bipyramids. Diaqua(dimethyl sulfoxide)tetrafluorozirconium dihydrate, $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$, crystallizes as a triclinic structure composed of isolated $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]$ pentagonal bipyramids with two non-coordinated H_2O molecules; the F—H and O—H hydrogen-bonding scheme has been determined.

Comment

The structure of tetrafluoro bis(dimethyl sulfoxide) zirconium (I) is built up from isolated $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$ bipolyhedra formed by F1—F1 edge-sharing of $[\text{ZrF}_5(\text{dmsO})_2]$ pentagonal bipyramids; the two molecules of dmsO are in the *trans* configuration (Fig. 1). The structure of diaqua tetrafluoro dimethyl sulfoxide zirconium dihydrate (II) is composed of isolated $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]$ pentagonal bipyramids and two non-coordinated water molecules (Fig. 2); the three-dimensional network is ensured by hydrogen bonding as shown in Fig. 3. The distances of possible hydrogen bonds are F1—H51 2.01(3), F2—H22 1.91(3), F3—H32 1.80(3), F4—H42 1.98(4), O4—H21 1.94(4), O4—H52 1.96(3) and O5—H31 1.80(4) Å.

The S—O distances [1.537(3) and 1.541(3) Å for (I), 1.539(1) Å for (II)] are longer than the value of 1.471 Å found for the free dmsO molecule (Viswamitra & Kannan,

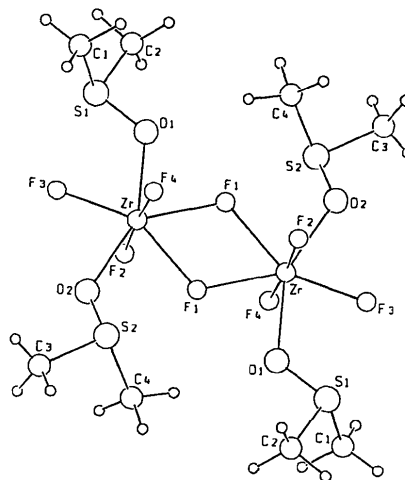


Fig. 1. View of $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$ showing atomic labelling scheme.

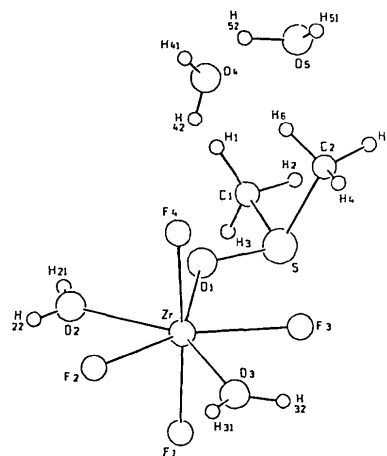


Fig. 2. View of $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ showing atomic labelling scheme.

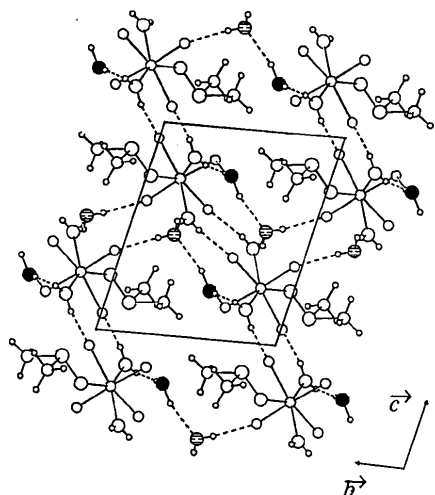


Fig. 3. View of $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ projected along (100). The hatched circle denotes O4 and the black circle O5.

1966) as a result of the coordination of the O atom with Zr atoms; the corresponding S—C distances are similar. The Zr—F and Zr—O distances (see Table 3) are very close to the values in the literature.

Experimental

Compound (I)

Crystal data

$[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$

$M_r = 646.96$

Monoclinic

$P2_1/n$

$a = 8.7974 (5) \text{ \AA}$

$b = 11.8717 (7) \text{ \AA}$

$c = 10.7790 (9) \text{ \AA}$

$\beta = 108.212 (5)^\circ$

$V = 1069.3 \text{ \AA}^3$

$Z = 2$

$D_x = 1.2009 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 42

reflections

$\theta = 15\text{--}17^\circ$

$\mu = 1.412 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism

$0.38 \times 0.19 \times 0.14 \text{ mm}$

Colourless

Data collection

Stoe-Siemens AED-2 diffractometer

$\theta/2\theta$ scans

Absorption correction:

Gaussian (SHELX76; Sheldrick, 1976)

$T_{\min} = 0.7193$, $T_{\max} = 0.8077$

4761 measured reflections

2991 independent reflections

2502 observed reflections [$I > 3.0\sigma(I)$]

$R_{\text{int}} = 0.0$

$\theta_{\max} = 30^\circ$

$h = -12 \rightarrow 12$

$k = 0 \rightarrow 16$

$l = 0 \rightarrow 15$

3 standard reflections

frequency: 60 min

intensity variation: 43.9%

Refinement

Refinement on F

Final $R = 0.023$

$wR = 0.023$

$S = 0.907$

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

$\Delta\rho_{\max} = 0.595 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.603 \text{ e \AA}^{-3}$

Extinction correction: none

2502 reflections

167 parameters

All H-atom parameters refined

Unit weights applied

Compound (II)

Crystal data

$[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

$M_r = 317.41$

Triclinic

$P\bar{1}$

$a = 7.357 (4) \text{ \AA}$

$b = 8.318 (4) \text{ \AA}$

$c = 9.627 (5) \text{ \AA}$

$\alpha = 99.95 (2)^\circ$

$\beta = 98.76 (2)^\circ$

$\gamma = 108.61 (2)^\circ$

$V = 536.15 \text{ \AA}^3$

$Z = 2$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection

Stoe-Siemens AED-2 diffractometer

$\theta/2\theta$ scans

Absorption correction:

Gaussian (SHELX76)

$T_{\min} = 0.7955$, $T_{\max} = 0.8601$

5076 measured reflections

4946 independent reflections

4559 observed reflections

[$I > 3.0\sigma(I)$]

$R_{\text{int}} = 0.0$

$\theta_{\max} = 36^\circ$

$h = -12 \rightarrow 12$

$k = -13 \rightarrow 13$

$l = 0 \rightarrow 15$

3 standard reflections

frequency: 60 min

intensity variation: 5.7%

Refinement

Refinement on F

Final $R = 0.021$

$wR = 0.021$

$S = 2.21$

4559 reflections

174 parameters

All H-atom parameters refined

Unit weights applied

$(\Delta/\sigma)_{\max} = 0.014$

$\Delta\rho_{\max} = 0.687 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.501 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for (I) and (II)

	$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			
	x	y	z	U_{eq}
$[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$				
Zr	0.32138 (2)	0.18397 (2)	0.26166 (5)	0.0213 (1)
Zr	0.46193 (3)	0.44936 (2)	0.14693 (3)	0.0197 (1)
S1	0.3480 (1)	0.1853 (1)	0.1801 (1)	0.0290 (5)
S2	0.5956 (1)	0.7016 (1)	0.2843 (1)	0.0290 (5)
F1	0.5182 (3)	0.5903 (2)	0.0417 (2)	0.038 (1)
F2	0.2334 (3)	0.4838 (2)	0.0665 (2)	0.047 (2)
F3	0.4177 (3)	0.3917 (2)	0.3057 (2)	0.042 (2)
F4	0.6942 (3)	0.4259 (2)	0.2218 (2)	0.048 (2)
O1	0.4229 (3)	0.2679 (2)	0.1059 (2)	0.039 (2)
O2	0.4847 (3)	0.5989 (2)	0.2724 (2)	0.032 (2)
C1	0.5131 (6)	0.1166 (4)	0.2945 (4)	0.045 (3)
C2	0.2783 (6)	0.0741 (3)	0.0650 (4)	0.043 (3)
C3	0.5896 (6)	0.7662 (4)	0.4326 (4)	0.044 (3)
C4	0.4814 (5)	0.8049 (3)	0.1747 (4)	0.035 (2)

[ZrF ₄ (dmsO)(H ₂ O) ₂].2H ₂ O				
S	0.49163 (6)	0.86829 (5)	0.13942 (4)	0.0265 (2)
F1	0.4827 (2)	0.3406 (2)	0.1566 (1)	0.0390 (9)
F2	0.2888 (2)	0.3887 (1)	0.3925 (1)	0.0407 (8)
F3	0.1903 (2)	-0.0055 (1)	0.0780 (1)	0.0384 (8)
F4	0.1623 (2)	0.0409 (2)	0.3763 (1)	0.046 (1)
O1	0.5011 (2)	0.0202 (2)	0.2603 (1)	0.0356 (9)
O2	0.5843 (2)	0.2977 (2)	0.4437 (2)	0.0381 (9)
O3	0.0568 (2)	0.2259 (2)	0.1546 (2)	0.042 (1)
O4	0.0636 (2)	0.7451 (2)	0.4741 (2)	0.039 (1)
O5	0.8918 (2)	0.4581 (2)	0.2272 (2)	0.048 (1)
C1	0.6967 (3)	0.8153 (3)	0.2116 (3)	0.050 (2)
C2	0.3011 (3)	0.6822 (3)	0.1562 (3)	0.046 (2)

Table 2. Selected bond distances (Å) and angles (°)

[Zr ₂ F ₈ (dmsO) ₄]			
Zr—F2	1.967 (2)	S1—O1	1.537 (3)
Zr—F4	1.968 (2)	S1—C1	1.783 (4)
Zr—F3	1.992 (2)	S1—C2	1.784 (4)
Zr—F1 ⁱ	2.147 (2)	S2—O2	1.541 (3)
Zr—F1	2.163 (2)	S2—C4	1.780 (3)
Zr—O2	2.203 (2)	S2—C3	1.789 (5)
Zr—O1	2.204 (2)		
F2—Zr—F4	175.6 (1)	F3—Zr—O2	75.77 (9)
F2—Zr—F3	90.2 (1)	F3—Zr—O1	77.08 (9)
F2—Zr—F1 ⁱ	90.2 (1)	F1 ⁱ —Zr—F1	64.75 (8)
F2—Zr—F1	88.7 (1)	F1 ⁱ —Zr—O2	137.68 (8)
F2—Zr—O2	89.3 (1)	F1 ⁱ —Zr—O1	69.48 (9)
F2—Zr—O1	92.3 (1)	F1—Zr—O2	72.93 (8)
F4—Zr—F3	93.2 (1)	F1—Zr—O1	134.22 (9)
F4—Zr—F1 ⁱ	88.60 (9)	O2—Zr—O1	152.8 (1)
F4—Zr—F1	86.91 (9)	O1—S1—C1	105.2 (2)
F4—Zr—O2	88.8 (1)	O1—S1—C2	102.7 (2)
F4—Zr—O1	91.2 (1)	O2—S2—C4	106.2 (1)
F3—Zr—F1 ⁱ	146.55 (8)	O2—S2—C3	102.7 (2)
F3—Zr—F1	148.69 (8)		

[ZrF ₄ (dmsO)(H ₂ O) ₂].2H ₂ O			
Zr—F4	1.990 (1)	Zr—O3	2.218 (2)
Zr—F1	1.991 (1)	Zr—O2	2.221 (1)
Zr—F3	2.022 (1)	S—O1 ⁱⁱ	1.539 (1)
Zr—F2	2.039 (1)	S—C2	1.777 (2)
Zr—O1	2.180 (2)	S—C1	1.779 (3)
F4—Zr—F1	176.32 (5)	F3—Zr—O1	75.89 (5)
F4—Zr—F3	91.70 (5)	F3—Zr—O3	71.43 (5)
F4—Zr—F2	84.50 (5)	F3—Zr—O2	144.27 (6)
F4—Zr—O1	88.87 (6)	F2—Zr—O1	140.51 (4)
F4—Zr—O3	90.25 (6)	F2—Zr—O3	71.82 (5)
F4—Zr—O2	92.60 (5)	F2—Zr—O2	72.71 (5)
F1—Zr—F3	91.67 (5)	O1—Zr—O3	147.27 (5)
F1—Zr—F2	91.92 (5)	O1—Zr—O2	68.76 (5)
F1—Zr—O1	93.39 (5)	O3—Zr—O2	143.95 (6)
F1—Zr—O3	89.42 (6)	O1 ⁱⁱ —S—C2	105.8 (1)
F1—Zr—O2	85.52 (5)	O1 ⁱⁱ —S—C1	102.2 (1)
F3—Zr—F2	143.02 (5)	C2—S—C1	98.4 (1)

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

The compound [Zr₂F₈(dmsO)₄] (I) was synthesized by recrystallization of ZrCl₄ in dmsO and subsequent fluorination by HF gas under a controlled atmosphere, or by recrystallization of ZrF₄ in dmsO as described by Muetterties (1960). The complex is hygroscopic. After addition of water to the ZrF₄ solution in dmsO at 423 K, (II) precipitates from the filtered solution at the ambient temperature; it is stable in air.

A small crystal of (I) was sealed in a 0.3 mm diameter Lindemann tube under a controlled atmosphere for the X-ray structure investigations. Stoe DIF4 software was used for data collection and cell refinement and Stoe REDU4 software for data reduction. The structure was solved and refined using SHELX76. SCHAKAL (Keller, 1989) was used for the molecular graphics.

The conditions limiting reflections led to the space groups P2₁/n for (I) and P1 for (II). Direct methods allowed the Zr

atoms to be located, other atoms were calculated from difference Fourier maps. The refinement used anisotropic thermal factors for all non-H atoms. The final atomic coordinates are listed in Table 1 while Table 2 gives the main interatomic distances in the two compounds.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55881 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1016]

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Structure of Bis[chloro{1-[(4-chloro-2-hydroxyphenyl)iminomethyl]naphthalen-2-olato-O,O',N'}]iron(III)]

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Abstract

Two identical [FeLCI] [$L = N$ -(4-chloro-2-hydroxyphenyl)-3-hydroxy-2-naphthaldimine] fragments, related by an inversion centre, are combined by the two bridging

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