

Di- μ -fluoro-bis[aqua-(dimethyl sulfoxide)-trifluorozirconium(IV)]

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$[\text{Zr}_2\text{F}_8(\text{dmsO})_2(\text{H}_2\text{O})_2]$, a dehydration product of $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$, crystallizes in the orthorhombic symmetry [space group *Cmca*, $a=7.8266(3)$ Å, $b=13.5847(5)$ Å, $c=15.6119(6)$ Å, and $Z=4$]. The structure, solved *ab initio* in direct space from X-ray powder diffraction data, is built up from $[\text{Zr}_2\text{F}_8\text{O}_4]$ bipolyhedra formed by edge sharing of $[\text{ZrF}_5\text{O}_2]$ pentagonal bipyramids (condensed from isolated $[\text{ZrF}_4\text{O}_3]$ pentagonal bipyramids in the precursor). Difficulties associated with a fortuitous hexagonal pseudosymmetry were surmounted. The dmsO departure at 220 °C leads to an amorphous phase. © 2010 International Centre for Diffraction Data. [DOI: 10.1154/1.3499814]

Key words: hybrid zirconium fluoride, dmsO, powder diffraction, crystal structure determination, *ab initio*

I. INTRODUCTION

Interest for metal-organic frameworks (MOFs) and the existence of such a zirconium-fluoride based compound $(\text{CN}_3\text{H}_6)_5(\text{H}_3\text{O})(\text{ZrF}_5)_6$ (Gerasimenko *et al.*, 1996) prompted us to invest more time on the structure solution of the thermal dehydration product of $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$. The latter is obtained by hydration of $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$, first synthesized by Muetterties (1960). The crystal structures of both these dmsO compounds were solved from single crystal data (Gao *et al.*, 1993). The structure of $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$, which was then published two more times (Alcock *et al.*, 1994; Il'in *et al.*, 1997), contains ZrF_5O_2 pentagonal bipyramids (sharing an edge, forming $\text{Zr}_2\text{F}_8\text{O}_4$ bipolyhedra) similar to the ZrF_7 ones three-dimensionally assembled by edges in the above-cited MOF. At the time of the powder thermodiffraction study (Gao, 1991), the structure of the title compound could not be solved due to the absence of a suitable single crystal. The aim of the present work is to solve the structure in direct space by taking advantage of the significant progress in powder diffraction methodologies in the past 20 years, as demonstrated during recent blind tests (Le Bail *et al.*, 2009).

II. EXPERIMENTAL

The title compound can be prepared in two ways, either (1) from the hygroscopic $[\text{Zr}_2\text{F}_8(\text{dmsO})_4]$ compound abandoned in air for some days or (2) from the $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ thermolysis. The latter was followed by TG analysis (Ar flow), DSC, and temperature resolved X-ray powder diffractometry (TXRD) (Siemens D5000 θ/θ diffractometer equipped with an Elphyse position-sensitive detector and an Anton Paar temperature attachment). For the TXRD, the sample was dusted on a platinum foil serving as heating source in a chamber pumped under vacuum, then filled with dried helium. A light He flow was maintained during the experiment. The time interval be-

tween successive powder patterns was 7200 s including a measuring time of 6600 s; the temperature was increased by steps of 10 °C starting from 30 up to 240 °C. Co $K\alpha$ radiation was used; measurements were from 10 to $140^\circ 2\theta$ by nearly $0.03^\circ 2\theta$ steps. A 3D view projection is shown in Figure 1. Under these conditions, the dehydration starts as soon as 40 °C and looks terminated at 50 °C, leading to a powder pattern identical (but with broader peak lineshapes) to that obtained from preparation (1). TGA and DSC (Figure 2) indicate a departure of three of the four water molecules, but due to the very different experimental conditions (10 °C/min), this is observed between 50 and 90 °C on the TGA corresponding to a sharp exothermic peak at 90 °C on the DSC. A next mass loss is observed on the TGA between 90 and 120 °C, corresponding to the fourth water molecule elimination (total water loss: 22.5%; expected: 22.7%). There are two broad exothermic peaks on the DSC at 118 and 131 °C. The dmsO elimination is seen in two steps between 240 and 330 °C on the TGA whereas at 220 °C, an amorphous material is observed on the TXRD after a long stability range of the title compound, showing only cell parameters increase due to thermal effects. This strong discrepancy between the TXRD and the TG-DSC experiment results

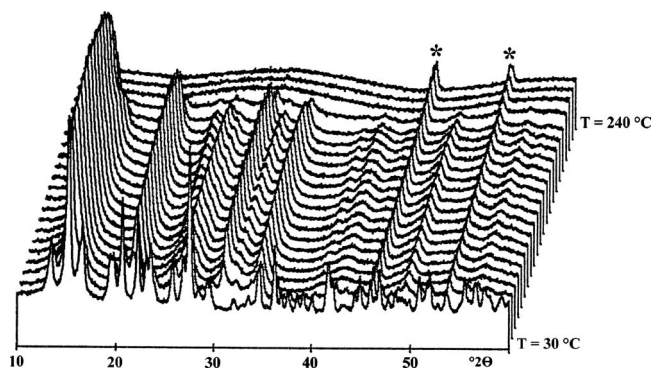


Figure 1. Projection of the X-ray powder diffraction patterns (Co $K\alpha$) as a function of the temperature (°C). The title compound, obtained at 40 °C from $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$, is stable up to 220 °C where it becomes amorphous. *: peaks from the platinum foil.

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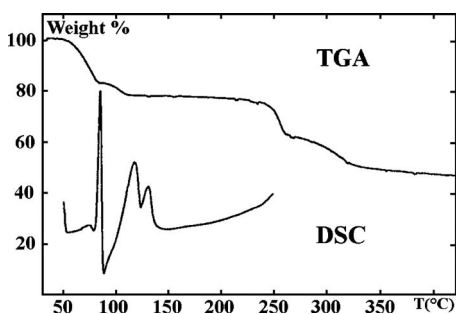


Figure 2. TG and DSC curves starting from $[\text{ZrF}_4(\text{dmso})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$.

led us to reproduce the DSC, stopping it at 90, 120, and 150 °C, recording X-ray patterns of the samples. A new crystalline anhydrous phase is observed at the latter temperature, and the title compound is observed at 90 °C and a phase mixture is observed at 120 °C with predominantly the title compound. The TG-DSC suggests that there could be two anhydrous phases appearing at the 10 °C/min heating rate; the X-rays may tell that the first anhydrous phase is hygroscopic and turns back to the title compound in air. More work would be needed in order to clarify all this; the powder pattern realized from the sample stopped at 150 °C during the DSC could not be indexed up to now. Finally, a powder pattern realized at room temperature from the sample collected at the TGA end (450 °C) allowed to recognize a mixture of the $\text{ZrF}_{3.33}\text{O}_{0.33}$ and $\text{Zr}_7\text{O}_9\text{F}_{10}$ compounds (PDF 00-036-1635 (ICDD, 2009) and PDF 00-027-0998 (ICDD, 2009), respectively). For the structural analysis, the sample from preparation (1) was selected due to its better crystallinity degree, recording a $\text{Cu K}\alpha$ powder pattern by using a Siemens D500 Bragg-Brentano diffractometer.

III. STRUCTURE DETERMINATION AND RIETVELD REFINEMENTS

At first sight, the powder pattern could be indexed in a hexagonal cell by the MCMAILLE software (Le Bail, 2004), with $a_{\text{H}}=7.84$ Å and, strange enough, $c_{\text{H}}=15.63$ Å $\sim 2a_{\text{H}}$, with figures of merit $R=9.2\%$, $\text{McM}_{20}=127$ (Le Bail, 2008), $M_{20}=29$ (de Wolff, 1968), and $F_{20}=38$ (0.0155, 34) (Smith and Snyder, 1979). However, the Le Bail fitting (Le Bail, 2005) applied for further evaluation of the reliability of the indexing and for intensity extraction was not fully satisfying at high angle ($R_{\text{p}}=10.0\%$; $R_{\text{WP}}=13.1\%$). No structure solution could be obtained in hexagonal symmetry, in which the only extinction condition was $00l, l=2n$ leading to either the $P6_322$, $P6_3/m$, or $P6_3$ space groups. Since four dmso molecules and four $[\text{ZrF}_5\text{O}_2]$ polyhedra are expected in the cell, they would have to occupy special positions which have site symmetries incompatible with the molecule and polyhedron shapes. More attention to the indexing suggested that the cell could be either monoclinic P , with $a_{\text{M}}=a_{\text{H}}$, $b_{\text{M}}=c_{\text{H}}$, $c_{\text{M}} \sim a_{\text{M}}$, and $b=120.13^\circ$ ($R=1.9\%$, $\text{McM}_{20}=52$, $M_{20}=25$, $F_{20}=34$ (0.0059, 98), $R_{\text{p}}=8.4\%$, and $R_{\text{WP}}=10.9\%$) or orthorhombic C centered with $a_{\text{O}}=a_{\text{H}}$, $b_{\text{O}} \sim a_{\text{H}}\sqrt{3}$, and $c_{\text{O}}=c_{\text{H}}$ ($R=2.9\%$, $\text{McM}_{20}=54$, $M_{20}=19$, $F_{20}=26$ (0.0061, 126), $R_{\text{p}}=7.0\%$, and $R_{\text{WP}}=9.8\%$). Due to the hexagonal pseudosymmetry and to $c_{\text{H}} \sim 2a_{\text{H}}$, it was hardly possible to deduce any space group in the C -centered orthorhombic cell. However,

TABLE I. Experimental and Rietveld refinement details for $[\text{Zr}_2\text{F}_8(\text{dmso})_2(\text{H}_2\text{O})_2]$.

Diffractometer	Siemens D500
Geometry	Bragg-Brentano
Radiation type	$\text{Cu K}\alpha$
Wavelengths (Å)	1.540 56, 1.544 33
Pattern range (2θ)	5 to 120
Step size (2θ)	0.02°
Chemical formula	$\text{C}_4\text{H}_{16}\text{F}_8\text{O}_4\text{S}_2\text{Zr}_2$
Space group	<i>Cmca</i>
	<i>a</i>
Cell parameter (Å)	7.8266 (3)
	<i>b</i>
	13.5847 (5)
	<i>c</i>
	15.6119 (6)
Volume (Å ³)	1659.89 (11)
Z	4
No. of contributing reflections	671
No. of refined parameters	58 (total)
No. of atomic coordinate parameters	22
No. of restraints	15
No. of isotropic thermal parameters	5
No. of background parameters (interpolated from a set of points)	19
Profile shape	pseudo-Voigt
η	0.72 (1)
<i>U</i>	0.35 (1)
<i>V</i>	-0.248 (8)
<i>W</i>	0.071 (1)
Conventional Rietveld reliability factors	(Rietveld, 1969)
R_{p} (%)	10.2
R_{WP} (%)	12.8
R_{exp} (%)	2.61
R_{B} (%)	4.73
R_{F} (%)	2.97

in the monoclinic cell, extinction conditions were compatible with the $P2_1/n$ space group. The first structure solution attempts were done in this monoclinic cell, in direct space, from the $\text{Cu K}\alpha$ conventional laboratory data, applying the ESPOIR software (Le Bail, 2001). A $[\text{ZrF}_5\text{O}_2]$ pentagonal bipyramid and a SOC_2 triangle were moved in the cell, by a Monte Carlo process, up to obtain $R_{\text{p}} \sim 12\%$ from the powder pattern regenerated from the 600 first $|F_{\text{obs}}|$ extracted by the Le Bail fit, revealing readily $[\text{Zr}_2\text{F}_8(\text{dmso})_2(\text{H}_2\text{O})_2]$ bipolyhedra. The Rietveld (1969) refinement by using the FULLPROF software (Rodríguez-Carvajal, 1993) was conducted with care due to the high degree of overlapping using soft distance restraints. The S atom was showing abnormally high thermal motion. Checking the structure for missing symmetries by using the PLATON software (Spek, 2003), the orthorhombic C -centered cell was suggested as the most probable with a *Cmca* space group. Indeed, the transformation was made easily from the monoclinic solution, leading to a final model characterized by a disorder on the sulphur atoms which are statistically either above or below the OC_2 triangle lying in the mirror parallel to the bc plane. The H atoms of the water molecule were located on the Fourier difference map, but not those of the CH_3 groups which were suggested then by the SHELX software (Sheldrick, 2008), but not refined. The final R values are listed in Table I (see the

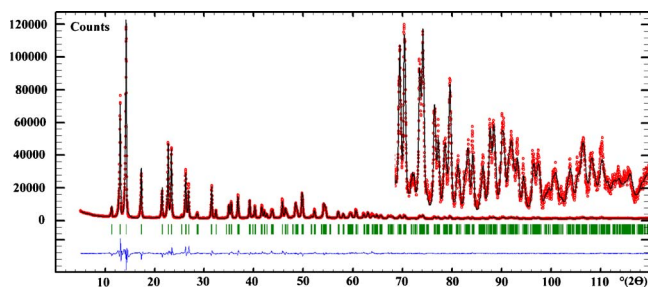


Figure 3. (Color online) Rietveld plot for $[\text{Zr}_2\text{F}_8(\text{dmsO})_2(\text{H}_2\text{O})_2]$.

Rietveld fit in Figure 3). Atomic coordinates, selected geometric parameters, and X-ray diffraction data are in Tables II–IV, respectively. Attempts to describe the structure with a full ordering of the S atom were unsuccessful. In the $Aba2$ noncentrosymmetric space group with same extinction as $Cmca$, the S atoms would all be either above or below the OC_2 plane, and the S atom thermal motion was still too high. In a pseudo-orthorhombic cell, with space group $C2/c$, both dmsO groups of the $[\text{Zr}_2\text{F}_8(\text{dmsO})_2(\text{H}_2\text{O})_2]$ bipolyhedra would be related by an inversion center, so that the S atoms would be ordered with half of them above the OC_2 plane, the other half below it. This did not decrease the sulphur thermal B values and doubled the number of reflections with exact overlapping. That solution remains possible; however, the best result with ESPOIR ($R_p=6\%$) was obtained in scratch mode (all atoms independent starting and moving at random in the cell) with this space group. In spite of the exact overlapping of a huge quantity of diffraction peaks, the complete molecule was revealed, showing how efficient the direct space approach can be.

IV. DISCUSSION

The $[\text{Zr}_2\text{F}_8(\text{dmsO})_2(\text{H}_2\text{O})_2]$ bipolyhedra (Figure 4) are interlinked by O-H...F bonds in layers parallel to the ac plane (Figure 5). The methyl groups of the dmsO molecules ensure H...F connections between the layers (Figure 6). Many layer structures show disorder problems so that the

TABLE III. Selected geometric parameters (Å, deg).

Zr-F1 2x	2.020 (4)	F2-F3	3.127 (8)
Zr-F2 2x	2.140 (2)	F2-O1	2.983 (2)
Zr-F3	2.004 (5)	F3-O2	2.719 (13)
Zr-O1	2.211 (2)	O1-O2	3.276 (8)
Zr-O2	2.232 (4)	O1-C1	2.623 (4)
F1-F2 ^a	2.543 (6)	O1-C2	2.623 (4)
F1-F3	2.835 (8)	O2-H2 2x	0.962 (10)
F1-O1	2.963 (7)	H2-H2 ^b	1.583 (10)
F1-O2	2.508 (5)	S-O1	1.541 (3)
F1-O2 ^c	2.497 (5)	S-C1	1.781 (4)
F1-H2 ^c	1.537 (15)	S-C2	1.780 (4)
F2-F2 ^a	2.312 (2)	C1-C2	2.729 (4)
F1-Zr-F1	143.7 (3)	F3-Zr-O1	174.7 (3)
F1-Zr-F2	140.6 (3)	F3-Zr-O2	79.7 (5)
F1-Zr-F3	89.4 (4)	O1-Zr-O2	95.0 (3)
F1-Zr-O1	88.8 (3)	H2-O2-H2 ^b	110.6 (13)
F1-Zr-O2	72.1 (2)	O2-H2-F1 ^c	174.9 (9)
F2-Zr-F2 ^a	65.38 (8)	O1-S-C1	104.0 (3)
F2-Zr-F3	97.9 (4)	O1-S-C2	104.1 (3)
F2-Zr-O1	86.53 (10)	C1-S-C2	100.0 (3)
F2-Zr-O2	147.3 (4)		

^aSymmetry code: $-x+1, -y+1, -z+1$.

^bSymmetry code: $-x+1, y, z$.

^cSymmetry code: $-x+3/2, y, -z+1/2$.

sulphur half occupancy above or below the OC_2 plane is understandable. The methyl H atoms could not be refined from these powder data. The C-H...F bonding scheme is thus not discussed. Moreover, the local disorder of the S atom plays a role on them, though it seems not to have an importance for the C atoms. Indeed, one should not expect much accuracy from that Rietveld refinement. Thanks to the soft constraints (1.54, 1.78, 2.62, 2.73, 0.96, 2.21, 2.00, 2.15, and 2.31 Å for S-O, S-C, O-C, C-C, O-H, Zr-O1/O2, Zr-F1/F3, Zr-F2, and F2-F2, respectively), with standard deviation of 0.003, taken from Gao *et al.*, (1993), the interatomic distances do not present unreasonable values. Otherwise, it is possible to get much lower R values but at the cost of dubious coordinates. In any case, the results shown here are the best obtainable from such powder data (though monochro-

TABLE II. Fractional atomic coordinates and isotropic displacement parameters.

	Wyckoff position	x	y	z	U_{iso}
Zr	8f	1/2	0.473 48 (11)	0.386 96 (9)	0.0165 (6)
F1	16g	0.7453 (4)	0.4579 (7)	0.3490 (4)	0.051 (2)
F2	8d	0.3523 (2)	1/2	1/2	0.051 (2)
F3	8f	1/2	0.6112 (3)	0.3410 (6)	0.051 (2)
O1	8f	1/2	0.316 74 (12)	0.4252 (2)	0.038 (4)
O2	8f	1/2	0.4431 (10)	0.246 48 (19)	0.038 (4)
H2	16g	0.6011 (9)	0.446 (7)	0.2115 (8)	0.080
S ^a	16g	0.4069 (5)	0.216 79 (18)	0.424 15 (17)	0.049 (3)
C1	8f	1/2	0.1531 (3)	0.336 01 (17)	0.068 (6)
H11 ^b	16g	0.6017	0.1101	0.3276	0.080
H12 ^b	8f	1/2	0.1956	0.2826	0.080
C2	8f	1/2	0.1506 (3)	0.510 79 (18)	0.068 (6)
H21 ^b	16g	0.6016	0.1043	0.5156	0.080
H22 ^b	8f	1/2	0.1869	0.5652	0.080

^aSite half occupied.

^bH atom at fixed position as guessed by SHELX (Sheldrick, 2008).

TABLE IV. X-ray diffraction data for $[\text{Zr}_2\text{F}_8(\text{dmsO})_2(\text{H}_2\text{O})_2]$ (Cu $K\alpha_1$).

$2\theta_{\text{obs}}$	d_{obs}	I_{obs}	h	k	l	$2\theta_{\text{cal}}$	d_{cal}	I_{cal}	$\Delta 2\theta$
11.326	7.8061	4.8	0	0	2	11.326	7.8061	5.8	0.000
13.023	6.7924	64.3	0	2	0	13.023	6.7924	59.2	0.000
14.224	6.2215	100.0	0	2	1	14.208	6.2284	4.5	0.016
			1	1	1	14.227	6.2201	100.0	-0.003
17.308	5.1193	23.5	0	2	2	17.292	5.1241	2.9	0.016
			1	1	2	17.307	5.1194	22.9	0.001
21.499	4.1298	14.6	0	2	3	21.493	4.1309	0.7	0.006
			1	1	3	21.506	4.1285	14.4	-0.007
22.718	3.9109	40.7	2	0	0	22.704	3.9133	25.2	0.014
			0	0	4	22.765	3.9030	19.2	-0.047
23.376	3.8023	38.4	1	3	1	23.381	3.8015	34.3	-0.005
25.429	3.4998	1.7	1	3	2	25.407	3.5027	0.1	0.022
			2	0	2	25.440	3.4983	0.6	-0.011
26.249	3.3923	26.5	0	4	0	26.218	3.3962	8.9	0.031
			2	2	0	26.261	3.3908	2.1	-0.012
			0	2	4	26.314	3.3841	8.1	-0.065
			1	1	4	26.324	3.3827	7.6	-0.075
26.836	3.3194	19.1	0	4	1	26.843	3.3185	13.2	-0.007
28.607	3.1178	3.0	1	3	3	28.486	3.1308	1.3	0.121
			0	4	2	28.641	3.1142	1.8	-0.034
31.508	2.8370	18.8	0	4	3	31.428	2.8441	2.2	0.080
			2	2	3	31.464	2.8409	0.4	0.044
			1	1	5	31.518	2.8362	14.0	-0.010
32.367	2.7637	4.5	2	0	4	32.370	2.7635	4.2	-0.003
34.497	2.5978	0.5	0	0	6	34.439	2.6020	0.1	0.058
34.993	2.5621	7.8	2	4	0	34.953	2.5649	0.6	0.037
			0	4	4	34.994	2.5620	3.0	-0.001
			2	2	4	35.026	2.5597	3.6	-0.033
35.446	2.5304	10.0	1	5	1	35.412	2.5327	2.6	0.034
			2	4	1	35.437	2.5310	0.9	0.009
			3	1	1	35.477	2.5282	4.9	-0.029
36.813	2.4395	14.1	1	3	5	36.771	2.4422	4.5	0.042
			1	5	2	36.832	2.4383	6.8	-0.019
39.154	2.2988	10.8	2	4	3	39.122	2.3007	0.3	0.032
			3	1	3	39.159	2.2986	6.2	-0.005
			0	4	5	39.159	2.2986	0.6	-0.005
			2	2	5	39.188	2.2969	2.5	-0.034
39.788	2.2637	1.7	0	6	0	39.780	2.2641	1.2	0.008
40.205	2.2411	7.8	0	6	1	40.214	2.2407	5.3	-0.009
			3	3	1	40.279	2.2372	1.4	-0.074
41.622	2.1681	7.9	0	6	2	41.493	2.1745	0.8	0.129
			3	3	2	41.556	2.1713	0.8	0.066
			1	3	6	41.627	2.1678	2.1	-0.005
			2	0	6	41.648	2.1667	3.1	-0.026
42.106	2.1442	4.9	1	5	4	42.100	2.1445	0.9	0.006
			2	4	4	42.121	2.1435	2.6	-0.015
42.623	2.1194	2.6	0	2	7	42.633	2.1190	0.9	-0.010
			1	1	7	42.640	2.1186	1.4	-0.017
43.583	2.0749	5.4	0	6	3	43.557	2.0761	0.8	0.026
			3	3	3	43.618	2.0734	2.1	-0.035
43.789	2.0656	5.0	0	4	6	43.793	2.0655	0.9	-0.004
			2	2	6	43.820	2.0642	2.9	-0.031
45.753	1.9814	12.3	1	5	5	45.721	1.9828	1.5	0.032
			3	1	5	45.773	1.9806	8.0	-0.020
46.374	1.9563	6.0	4	0	0	46.366	1.9567	3.7	0.008
46.680	1.9442	3.2	2	6	1	46.674	1.9445	1.7	0.006
48.433	1.8779	8.8	4	2	0	48.370	1.8802	4.0	0.063
			0	2	8	48.495	1.8756	4.9	-0.062
			1	1	8	48.502	1.8754	0.7	-0.069

TABLE IV. (Continued.)

$2\theta_{\text{obs}}$	d_{obs}	I_{obs}	h	k	l	$2\theta_{\text{cal}}$	d_{cal}	I_{cal}	$\Delta 2\theta$
48.740	1.8668	4.9	1	7	1	48.648	1.8701	1.2	0.092
			3	5	1	48.698	1.8683	0.9	0.042
			4	2	1	48.742	1.8667	0.5	-0.002
			0	4	7	48.811	1.8642	1.1	-0.071
49.749	1.8312	16.1	2	2	7	48.836	1.8633	1.8	-0.096
			2	6	3	49.669	1.8340	1.1	0.080
			0	6	5	49.700	1.8329	1.6	0.049
			1	7	2	49.754	1.8311	6.3	-0.005
			3	3	5	49.755	1.8310	2.7	-0.006
			3	5	2	49.803	1.8294	1.8	-0.054
51.604	1.7697	1.6	1	5	6	49.864	1.8273	2.1	-0.115
			2	4	6	49.883	1.8266	3.3	-0.134
			3	5	3	51.605	1.7696	0.4	-0.001
			4	2	3	51.647	1.7683	0.7	-0.043
			2	6	4	52.184	1.7514	1.4	0.051
			4	0	4	52.255	1.7492	3.1	-0.020
54.111	1.6935	9.4	1	3	8	52.327	1.7469	0.2	-0.092
			2	0	8	52.344	1.7464	0.8	-0.109
			4	2	4	54.096	1.6939	5.0	0.015
			0	4	8	54.160	1.6920	0.9	-0.049
54.489	1.6826	6.3	2	2	8	54.183	1.6914	2.8	-0.072
			0	8	1	54.296	1.6881	1.9	0.193
			4	4	1	54.388	1.6855	1.2	0.101
			2	4	7	54.475	1.6830	2.4	0.014
57.015	1.6139	4.4	1	1	9	54.561	1.6806	2.9	-0.072
			0	8	3	57.000	1.6143	2.0	0.015
			1	7	5	57.055	1.6129	0.6	-0.040
			3	5	5	57.100	1.6117	2.3	-0.085
58.055	1.5875	3.0	0	6	7	57.998	1.5889	0.6	0.057
			1	3	9	58.103	1.5862	2.7	-0.048
			4	4	4	59.385	1.5550	1.8	-0.002
59.383	1.5551	3.5	1	5	8	59.451	1.5535	0.4	-0.068
			2	4	8	59.467	1.5531	0.7	-0.084
			2	8	1	59.595	1.5501	0.8	0.039
59.634	1.5487	3.1	5	1	1	59.709	1.5474	1.8	-0.075
			3	7	2	60.588	1.5270	3.0	0.011
60.599	1.5268	6.1	1	7	6	60.642	1.5258	1.8	-0.043
			3	5	6	60.684	1.5248	1.1	-0.085
			4	2	6	60.722	1.5240	0.6	-0.123

matic Cu $K\alpha_1$ radiation may help a bit) showing isotropic line broadening due to the fragmentation associated with the probably topotactic reaction of dehydration from the $[\text{ZrF}_4(\text{dmsO})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ precursor. From the TGA and

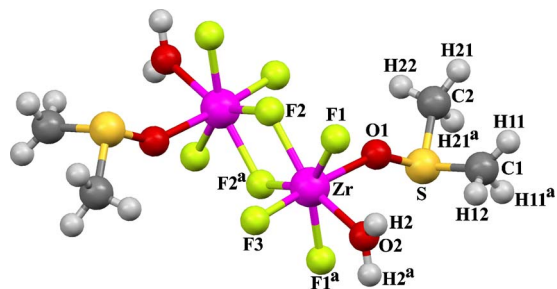


Figure 4. (Color online) The di- μ -fluoro-bis[aqua-(dimethyl sulfoxide)-trifluorozirconium(IV)] molecule with atom numbering. Symmetry code: $-x+1, y, z$.

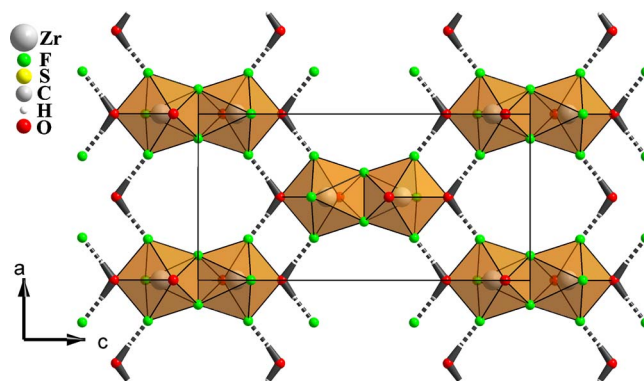


Figure 5. (Color online) View of a layer formed by $[\text{Zr}_2\text{F}_8\text{O}_2(\text{H}_2\text{O})_2]$ bipolyhedra interconnected by O-H...F bonds. dmsO is omitted for the sake of clarity.

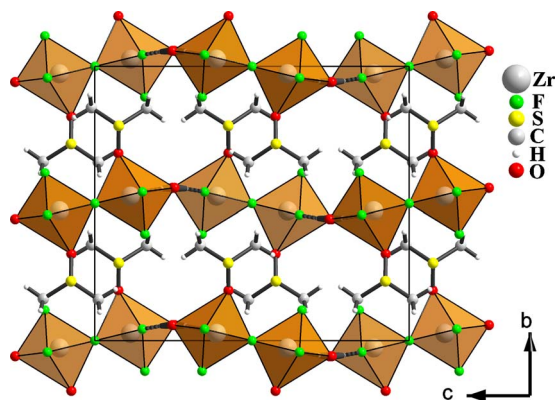


Figure 6. (Color online) Projection of the structure along the *a* axis, showing the dmsol molecules interconnecting the layers in Figure 5. The small cavity detected by PLATON at $x=1/4, y=0.292, z=1/4$ (*8e* Wyckoff position) is obvious.

DSC experiments, the two water molecules not bonded to Zr are first lost together with one of the two bonded ones, leading to the condensation from $[\text{ZrF}_4\text{O}(\text{H}_2\text{O})_2]$ pentagonal bipyramids of the precursor (Figure 7) into the $[\text{Zr}_2\text{F}_8\text{O}_2(\text{H}_2\text{O})_2]$ bipolyhedra of the title compound. There are two possibilities to form the bipolyhedra, as seen in Figure 7 [noted (a) and (b)], since the pentagonal bipyramids form infinite chains with O-H...F connections. In both cases the dmsol will be *in trans*-position as observed in the title compound. The (a) possibility lets the remaining water molecule adjacent to the dmsol oxygen atom, as found in the title compound, and is thus more probable. However, the dmsol oxygen atom belongs to the pentagon in the precursor and is one apex of the bipyramid in $[\text{Zr}_2\text{F}_8(\text{dmsol})_2(\text{H}_2\text{O})_2]$, so that there must be other displacements. There is the same problem with the hydrolysis of $[\text{Zr}_2\text{F}_8(\text{dmsol})_4]$ (mode of preparation 1), where the bipolyhedra must lose half the dmsol molecules, replace their oxygen atom by water, plus some displacements as well. Figure 5 suggests that another condensation would be easy by the departure of the ultimate water molecule in the title compound, leading to a compact layer of pentagonal bipyramids sharing three of their edges and to a 3D net after the dmsol departure. In the TXRD conditions an amorphous compound is obtained, which could

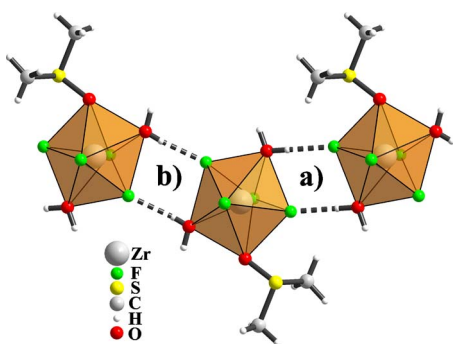


Figure 7. (Color online) $[\text{ZrF}_4\text{O}(\text{H}_2\text{O})_2]$ pentagonal bipyramids in the $[\text{ZrF}_4(\text{dmsol})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ precursor (Gao *et al.*, 1993). During dehydration, the two water molecules not bonded to Zr are lost, and also one of the two bonded ones leading to the condensation into the $[\text{Zr}_2\text{F}_8\text{O}_2(\text{H}_2\text{O})_2]$ bipolyhedra of the title compound. Such a condensation can occur either at positions (a) or (b).

be a MOF. More work would be needed to test if it has some properties of gas absorption/desorption. Concerning the title compound, when searching for voids, the PLATON software suggested a small cavity at $x=1/4, y=0.292, z=1/4$ (*8e* Wyckoff position) at 2.74 Å from the first neighbours (F1) which is a bit short for inserting a water molecule (attempts to add something there during the refinements failed). The CIF was deposited (No. 3000001) at the crystallography open database (www.crystallography.net) (Gražulis *et al.*, 2009).

V. CONCLUSION

It is shown that the potential of producing new hybrid compounds and eventually MOFs based on zirconium fluorides is far from being completely explored. In the absence of a suitable single crystal, which is frequently a consequence of thermolysis, modern powder diffraction methodologies have the power to reveal crystal structures which would stay ignored without some efforts. However, the other phases observed to occur with different heating rates remain uncharacterized.

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