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Acta Cryst. (1994). **C50**, 1540–1541

Di- μ -fluoro-bis[bis(*N,N*-dimethylformamide)trifluorozirconium(IV)]

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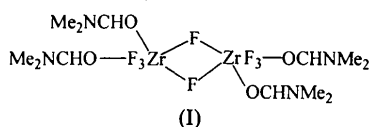
(Received 17 March 1994; accepted 26 May 1994)

Abstract

The title compound, [ZrF₃(C₃H₇NO)₂(μ -F)]₂, is a centrosymmetric fluorine-bridged dimer. The seven-coordinate Zr atoms are in a pentagonal bipyramidal environment with F atoms above and below the pentagonal plane. The average Zr—F bridging distance of 2.147 (4) Å is significantly longer than the mean terminal distance of 1.962 (4) Å.

Comment

The structure of the title compound (I) has been determined as part of a continuing study of ZrF₄ adducts (Alcock, Errington, Golby, Patterson & Wallbridge, 1994). The compound obtained by refluxing ZrF₄ with *N,N*-dimethylformamide (dmf) has been reported (Muettterties, 1960) as a 1:1 adduct, but the material investigated in this work is clearly the 1:2 adduct (I).



The molecular structure is shown in Fig. 1. It consists of two pentagonal bipyramidal units linked *via* two F-atom bridges to give a centrosymmetric dimer. The equatorial ligand donor atoms are almost coplanar: F3 and O21 are 0.038 (5) and 0.056 (3) Å, respectively, above the plane of Zr1, F4, Zr1ⁱ and F4ⁱ, while O11 is 0.073 (5) Å below the plane. The axial F atoms, F1 and F2, are displaced 1.952 (4) Å from this plane. The mean length of the terminal Zr—F bonds is 1.962 (4) Å, while, as expected, the bridging Zr—F bonds are longer, averaging 2.147 (4) Å.

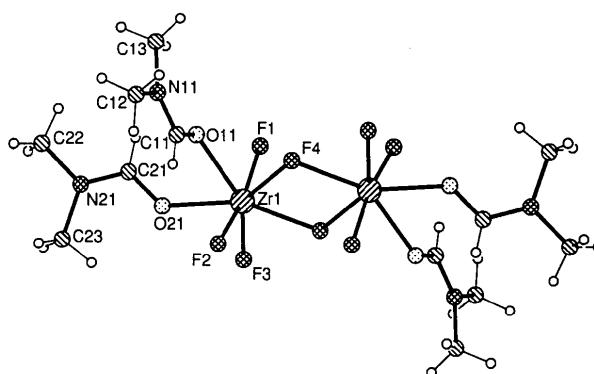


Fig. 1. View of the molecule showing the non-H-atom labelling.

Relatively few structures have been reported involving coordinated dmfm, but in all cases it bonds through the O atom (Goggin, 1987). In the title compound, the Zr1—O21 and Zr1—O11 distances [2.227 (3) and 2.239 (4) Å, respectively] are similar to those reported for the Zr—O bond lengths [2.253 (2) and 2.198 (2) Å] in CpZrCl₃(dmfm)₂ (Erker *et al.*, 1990). Furthermore, the ligand bond lengths C11—N11 and C21—N21 of 1.298 (6) and 1.304 (5) Å, respectively, are indicative of some double-bond character, and agree with earlier results (Holt, Alcock, Sumner & Asplund, 1979; Erker *et al.*, 1990). Two dmfm ligands are located almost along the Zr1···Zr1ⁱ axis [Zr1ⁱ···Zr—O21 = 176.51 (8)°], with the other pair at an angle of 103.65 (12)° to this axis. The coordination sites for the dmfm ligands contrast with those reported previously (Alcock, Errington, Golby, Patterson & Wallbridge, 1994) for the analogous dimethyl sulfoxide complex [ZrF₄(Me₂SO)₂]₂, where the Zr···Zr—O angles are all about 103°.

Experimental

The complex was prepared by refluxing ZrF₄ in *N,N*-dimethylformamide (Muettterties, 1960) and allowed to crystallize upon cooling. The complex decomposes slowly in air and was, therefore, covered in a layer of Nujol prior to fixing onto a quartz fibre. Decomposition was further reduced by collecting the data with the crystal at 230 K under a stream of dry air.

Crystal data

[ZrF₄(C₃H₇NO)₂]

M_r = 313.41

Triclinic

P $\bar{1}$

a = 8.369 (8) Å

b = 8.899 (7) Å

c = 9.501 (12) Å

α = 96.40 (8)°

β = 114.53 (9)°

γ = 115.50 (6)°

V = 543.5 (10) Å³

Z = 2

D_x = 1.915 Mg m⁻³

Mo *K* α radiation

λ = 0.71073 Å

Cell parameters from 18 reflections

θ = 8–9°

μ = 1.052 mm⁻¹

T = 230 (2) K

Flat block

0.36 × 0.09 × 0.06 mm

Colourless

Data collection

Siemens R3m diffractometer	$R_{\text{int}} = 0.0487$
ω - 2θ scans	$\theta_{\text{max}} = 25.05^\circ$
Absorption correction:	$h = -9 \rightarrow 1$
Analytical	$k = -9 \rightarrow 10$
$T_{\text{min}} = 0.84$, $T_{\text{max}} = 0.94$	$l = -10 \rightarrow 11$
2343 measured reflections	3 standard reflections
1921 independent reflections	monitored every 200 reflections
1778 observed reflections	intensity variation: none
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = -0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0382$	$\Delta\rho_{\text{max}} = 1.37 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.1115$	$\Delta\rho_{\text{min}} = -1.19 \text{ e } \text{\AA}^{-3}$
$S = 1.064$	Extinction correction: none
1920 reflections	Atomic scattering factors
146 parameters	from <i>International Tables</i>
Only coordinates of H atoms	for <i>Crystallography</i> (1992),
refined, $U(\text{H}) \approx 1.5U_{\text{eq}}(\text{C})$	Vol. C, Tables 4.2.6.8 and
$w = 1/[\sigma^2(F_o^2) + (0.0936P)^2$	6.1.1.4)
$+ 0.1370P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Zr1	0.05302 (5)	0.85504 (4)	0.90341 (4)	0.0201 (2)
F1	-0.1682 (4)	0.6443 (3)	0.8975 (3)	0.0368 (6)
F2	0.3113 (4)	1.0630 (3)	0.9512 (3)	0.0344 (6)
F3	-0.0915 (4)	0.8016 (4)	0.6637 (3)	0.0415 (7)
F4	0.1042 (4)	1.0057 (3)	1.1297 (3)	0.0299 (5)
O11	0.2570 (4)	0.8117 (3)	1.1157 (3)	0.0257 (6)
O21	0.1363 (5)	0.6832 (4)	0.7990 (4)	0.0322 (7)
N11	0.5499 (5)	0.9011 (4)	1.3536 (4)	0.0259 (7)
N21	0.2400 (5)	0.4946 (4)	0.7669 (4)	0.0269 (7)
C11	0.4448 (6)	0.9184 (5)	1.2175 (5)	0.0257 (8)
C12	0.7687 (6)	1.0330 (6)	1.4709 (6)	0.0339 (9)
C13	0.4536 (7)	0.7467 (6)	1.3958 (5)	0.0332 (10)
C21	0.1640 (6)	0.5614 (5)	0.8314 (5)	0.0266 (8)
C22	0.2734 (8)	0.3530 (6)	0.8080 (6)	0.0374 (10)
C23	0.3081 (8)	0.5649 (6)	0.6565 (6)	0.0413 (11)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Zr1—F1	1.962 (3)	O11—C11	1.247 (6)
Zr1—F3	1.962 (4)	O21—C21	1.247 (5)
Zr1—F2	1.963 (4)	N11—C11	1.298 (6)
Zr1—F4 ⁱ	2.125 (3)	N11—C12	1.462 (6)
Zr1—F4	2.168 (4)	N11—C13	1.462 (5)
Zr1—O21	2.227 (3)	N21—C21	1.304 (5)
Zr1—O11	2.239 (4)	N21—C22	1.463 (5)
F4—Zr1 ⁱ	2.125 (3)	N21—C23	1.467 (6)
F1—Zr1—F3	95.3 (2)	F2—Zr1—O21	88.25 (15)
F1—Zr1—F2	168.25 (11)	F4—Zr1—O11	71.44 (13)
F3—Zr1—F2	95.3 (2)	O21—Zr1—O11	73.23 (14)
F1—Zr1—F4	88.6 (2)	Zr1 ⁱ —F4—Zr1	114.80 (13)
F2—Zr1—F4	86.3 (2)	C11—O11—Zr1	126.4 (3)
F4 ⁱ —Zr1—F4	65.20 (13)	C21—O21—Zr1	134.0 (3)
F1—Zr1—O21	89.80 (14)	O11—C11—N11	124.4 (4)
F3—Zr1—O21	73.93 (13)	O21—C21—N21	122.9 (4)

Symmetry code: (i) $-x, 2 - y, 2 - z$.

Data collection and cell refinement: Siemens R3m software. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1994).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: MU1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). **C50**, 1541–1544

Pentaaquadioxouranium(VI) Triflate–18-Crown-6

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(Received 11 August 1993; accepted 7 February 1994)

Abstract

The uranyl ion in pentaaquadioxouranium(VI) bis-(trifluoromethanesulfonate)-1,4,7,10,13,16-hexaoxacyclooctadecane, $[\text{UO}_2(\text{H}_2\text{O})_5](\text{CF}_3\text{SO}_3)_2 \cdot \text{C}_{12}\text{H}_{24}\text{O}_6$, is equatorially surrounded by five O atoms from water molecules. The CF_3SO_3^- ions and the crown ether are not part of the uranyl coordination polyhedron but are linked to the U atom *via* hydrogen bonds.

Comment

As part of our studies of uranyl macrocyclic complexes, we have recently reported the structures of UO_2 -crown ether (Deshayes, Keller, Lance, Navaza, Nierlich & Vigner, 1994) and UO_2 -azacrown (Nierlich, Sabattie, Keller, Lance & Vigner, 1994) inclusion compounds obtained in organic solution.