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A Complex Between Uranyl Trifluoromethanesulfonate Hydrate and Benzo-15-crown-5

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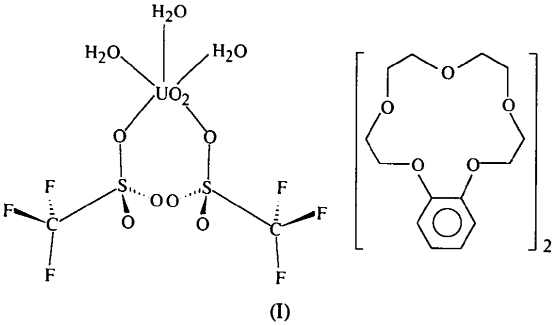
Abstract

In triaquadioxobis(trifluoromethanesulfonato)uranium(VI)–benzo-15-crown-5 (1/2), $[UO_2(CF_3SO_3)_2(H_2O)_3].2C_{14}H_{20}O_5$, the uranyl ion is in a pentagonal pseudo-planar equatorial environment, consisting of two O atoms from two trifluoromethanesulfonate (triflate) ions and three from water molecules. The coordination of $CF_3SO_3^-$ is particularly notable owing to the poor coordinating character of this ion. Two molecules of benzo-15-crown-5 are hydrogen bonded to the water molecules (one water molecule bridging) without any direct interaction with the uranyl moiety.

Comment

The inclusion of the uranyl ion into the cavity of crown ethers and azacrowns can only be achieved in a poorly coordinating medium (solvent and counterion); in other conditions, complexes in which the macrocycles are only hydrogen bonded to the uranyl coordination-sphere atoms are obtained (Thuéry, Keller, Lance, Vigner & Nierlich, 1995, and references therein). Several examples have been given of such hydrogen-bonded out-of-cavity complexes in which the coordination to water molecules or counterions such as nitrate or chlorine prevents inclusion. Furthermore, an 18-crown-6-type cavity size has been shown to be a prerequisite for uranyl inclusion (Deshayes, Keller, Lance, Navaza, Nierlich & Vigner, 1994); in particular, no uranyl inclusion is observed with 15-crown-5 or benzo-15-crown-5, even in a poorly coordinating medium. In this paper we report the structure of the out-of-cavity complex $[UO_2(CF_3SO_3)_2(H_2O)_3].2C_{14}H_{20}O_5$, (I). *ORTEPII* (Johnson, 1976) drawings of the asymmetric unit and of the crystal packing are shown in Figs. 1 and 2.



(I)

The U atom is located on a site without any local symmetry. The linear uranyl ion (with normal geometrical features) is surrounded in its equatorial plane by five donor O atoms, one from each $CF_3SO_3^-$ counterion and three from the water molecules. The U—O(water) distances [2.383 (9), 2.42 (1) and 2.424 (9) Å] are comparable to those found in pentaaqua uranyl complexes (Alcock & Esperås, 1977; Deshayes, Keller, Lance, Nierlich & Vigner, 1994). The U—O(triflate) distances [2.38 (1) and 2.392 (9) Å] are in agreement with those determined by EXAFS spectrometry in $[UO_2(CF_3SO_3)_2(CH_3CN)_3]$ [2.400 (1) in the solid state, 2.36 (1) Å in solution] and in out-of-cavity complexes with various crown ethers (ranging between 2.30 and 2.39 Å) (Deshayes, Keller, Lance, Nierlich & Vigner, 1994). The five O-atom donors are in a plane with a maximum deviation of ±0.06 (1) Å, the U atom being 0.013 (1) Å from this mean plane.

Two crystallographically independent crown ethers are present in the asymmetric unit. Each of them displays short intermolecular contacts (between 2.66 and 2.86 Å) with two water molecules, which suggests the formation of hydrogen bonds. One of the water molecules is possibly bonded to both crown ethers. One of the two crown ethers (corresponding to O atoms O17–O21) adopts the conformation $g^-g^+g^-g^-$ for the O—C—C—O torsion angles (except the one corresponding to the aromatic cycle) with two C—O—C—C torsion angles in a *gauche* rather than *anti* conformation [−74 (2) and −76 (2)°]. The other crown ether (corresponding to O atoms O12–O16) adopts a more distorted conformation, with one O—C—C—O torsion angle of 10 (4)° and one C—O—C—C of 66 (2)°. For both crown ethers, the dihedral angle between the aromatic ring and the mean plane defined by the five O atoms is rather high [65.3 (4) and 76.6 (4)°, respectively].

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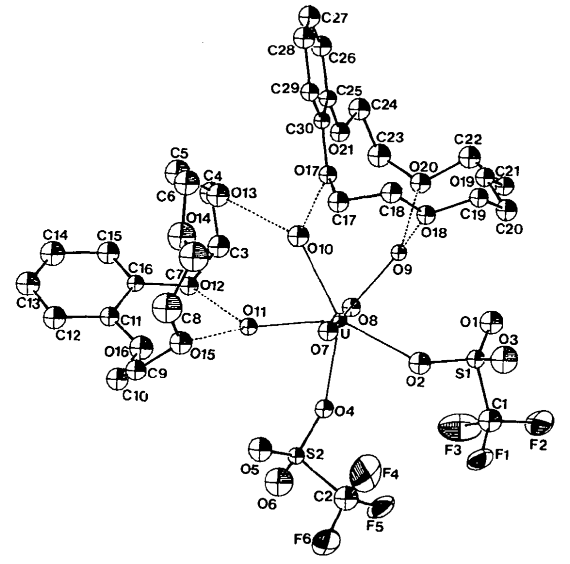

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with atomic labelling (ellipsoids drawn at the 40% probability level).

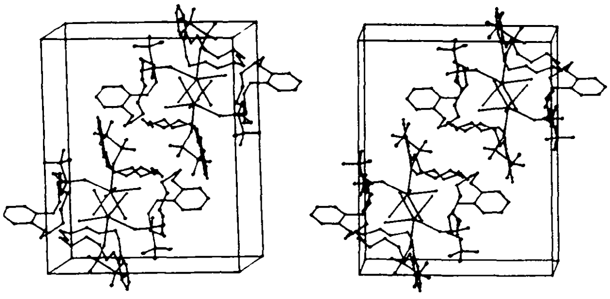

Fig. 2. Stereoview of the crystal packing of the title compound parallel to the *ac* plane.

Experimental

Crystals were obtained by slow evaporation of a water/acetonitrile solution of benzo-15-crown-5 and uranyl bis(trifluoromethanesulfonate).

Crystal data

$[UO_2(CF_3SO_3)_2(H_2O)_3]$.-
$2C_{14}H_{20}O_5$
$M_r = 1158.84$
Monoclinic
$P2_1/n$
$a = 15.749\,(4)$ Å
$b = 14.283\,(6)$ Å
$c = 19.010\,(5)$ Å
$\beta = 90.35\,(2)°$
$V = 4276\,(4)$ Å^3
$Z = 4$
$D_x = 1.800$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–12°
$\mu = 3.79$ mm^{-1}
$T = 293$ K
Irregular
0.3 × 0.25 × 0.15 mm
Yellow–green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.39$, $T_{\max} = 0.65$
4535 measured reflections
3978 independent reflections

2521 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.02$
$\theta_{\max} = 20°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.050$
$S = 2.02$
2521 reflections
286 parameters
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.66$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$B_{\rm iso}$ for C, O; $B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for U, S and F atoms.

	x	y	z	$B_{\rm iso}/B_{\rm eq}$
U	0.22609 (3)	0.11385 (4)	0.28612 (2)	2.21 (1)
S1	0.0003 (2)	0.1272 (3)	0.3326 (2)	3.47 (9)
S2	0.2913 (2)	0.1011 (3)	0.4722 (2)	3.02 (8)
F1	−0.0130 (7)	0.1062 (8)	0.4667 (5)	8.7 (3)
F2	−0.1019 (7)	0.198 (1)	0.4203 (6)	14.2 (4)
F3	0.030 (1)	0.2408 (8)	0.4338 (6)	12.2 (4)
F4	0.1655 (8)	−0.010 (1)	0.4846 (7)	12.8 (4)
F5	0.1505 (7)	0.119 (1)	0.5378 (5)	12.8 (4)
F6	0.2315 (8)	0.021 (1)	0.5824 (5)	13.2 (4)
O1	−0.0174 (7)	0.2031 (8)	0.2871 (5)	5.9 (3)
O2	0.0898 (7)	0.1051 (7)	0.3396 (5)	5.4 (2)
O3	−0.0524 (8)	0.0466 (9)	0.3272 (7)	7.9 (3)
O4	0.2494 (6)	0.1351 (6)	0.4095 (5)	3.8 (2)
O5	0.3454 (7)	0.0239 (8)	0.4611 (6)	6.3 (3)
O6	0.3232 (9)	0.174 (1)	0.5136 (7)	8.8 (4)
O7	0.2346 (6)	−0.0066 (7)	0.2939 (5)	4.4 (2)
O8	0.2173 (6)	0.2344 (7)	0.2762 (4)	3.9 (2)
O9	0.1301 (5)	0.0950 (6)	0.1898 (4)	2.8 (2)
O10	0.2978 (7)	0.1114 (7)	0.1739 (5)	5.0 (2)
O11	0.3783 (6)	0.1272 (6)	0.3026 (4)	3.5 (2)
O12	0.4905 (6)	0.2733 (7)	0.2586 (5)	3.8 (2)
O13	0.4389 (7)	0.1993 (8)	0.1285 (6)	5.9 (3)
O14	0.4846 (8)	0.022 (1)	0.1757 (7)	8.6 (4)
O15	0.4769 (7)	−0.0230 (8)	0.3183 (5)	5.4 (3)
O16	0.5553 (7)	0.1525 (8)	0.3382 (6)	6.3 (3)
O17	0.2419 (6)	−0.0271 (6)	0.0798 (5)	3.5 (2)
O18	0.0740 (6)	−0.0623 (7)	0.1263 (4)	3.5 (2)
O19	−0.0076 (6)	0.0992 (7)	0.0818 (5)	3.9 (2)
O20	0.1092 (6)	0.2428 (7)	0.1041 (5)	4.2 (2)
O21	0.2366 (6)	0.1387 (6)	0.0326 (4)	3.9 (2)
C1	−0.024 (1)	0.171 (1)	0.4177 (8)	5.7 (4)
C2	0.202 (1)	0.056 (1)	0.5239 (9)	6.0 (4)
C3	0.450 (1)	0.329 (1)	0.2060 (7)	5.4 (4)
C4	0.460 (1)	0.297 (1)	0.1349 (8)	6.1 (4)
C5	0.501 (1)	0.142 (1)	0.098 (1)	7.4 (5)
C6	0.482 (1)	0.044 (1)	0.1066 (9)	7.5 (5)
C7	0.459 (1)	−0.069 (2)	0.196 (1)	9.9 (7)
C8	0.489 (1)	−0.087 (1)	0.266 (1)	10.4 (7)
C9	0.544 (1)	0.001 (2)	0.361 (1)	10.5 (7)
C10	0.585 (2)	0.066 (2)	0.371 (1)	11.6 (8)
C11	0.613 (1)	0.200 (1)	0.3011 (7)	4.0 (3)
C12	0.701 (1)	0.190 (1)	0.3028 (8)	5.8 (4)
C13	0.750 (1)	0.248 (1)	0.2629 (9)	6.6 (5)
C14	0.718 (1)	0.318 (1)	0.2258 (8)	6.4 (5)

C15	0.629 (1)	0.330 (1)	0.2227 (8)	5.2 (4)
C16	0.5782 (9)	0.269 (1)	0.2587 (7)	3.2 (3)
C17	0.2143 (9)	−0.114 (1)	0.1096 (8)	4.7 (4)
C18	0.1256 (9)	−0.131 (1)	0.0939 (8)	5.1 (4)
C19	−0.0108 (9)	−0.060 (1)	0.1009 (7)	4.1 (3)
C20	−0.049 (1)	0.026 (1)	0.1201 (8)	5.1 (4)
C21	−0.0318 (9)	0.193 (1)	0.0988 (7)	4.2 (4)
C22	0.032 (1)	0.254 (1)	0.0687 (8)	5.3 (4)
C23	0.181 (1)	0.284 (1)	0.0708 (8)	5.7 (4)
C24	0.213 (1)	0.231 (1)	0.0088 (8)	5.5 (4)
C25	0.2529 (9)	0.070 (1)	−0.0178 (7)	3.4 (3)
C26	0.267 (1)	0.086 (1)	−0.0872 (8)	4.6 (4)
C27	0.282 (1)	0.008 (1)	−0.1307 (8)	5.2 (4)
C28	0.282 (1)	−0.077 (1)	−0.1076 (8)	5.1 (4)
C29	0.2690 (9)	−0.092 (1)	−0.0365 (7)	4.0 (3)
C30	0.2542 (8)	−0.019 (1)	0.0076 (7)	2.9 (3)

Table 2. *Selected geometric parameters* (Å, °)

U—O7	1.73 (1)	U—O8	1.74 (1)
U—O2	2.38 (1)	U—O4	2.392 (9)
U—O9	2.383 (9)	U—O10	2.42 (1)
U—O11	2.424 (9)		
O7—U—O8	178.7 (4)	O7—U—O2	88.9 (5)
O7—U—O4	91.8 (4)	O7—U—O9	90.1 (4)
O7—U—O10	91.4 (4)	O7—U—O11	89.5 (4)
O8—U—O2	91.5 (4)	O8—U—O4	89.6 (4)
O8—U—O9	88.8 (4)	O8—U—O10	87.5 (4)
O8—U—O11	90.8 (4)	O2—U—O4	73.8 (4)
O2—U—O9	75.7 (3)	O9—U—O10	67.6 (3)
O10—U—O11	69.4 (3)	O11—U—O4	73.6 (3)
S1—O1	1.41 (1)	S1—O2	1.45 (1)
S1—O3	1.42 (1)	S1—C1	1.78 (2)
C1—F1	1.32 (2)	C1—F2	1.28 (2)
C1—F3	1.35 (2)		
S2—O4	1.44 (1)	S2—O5	1.41 (1)
S2—O6	1.40 (2)	S2—C2	1.83 (2)
C2—F4	1.33 (2)	C2—F5	1.25 (2)
C2—F6	1.30 (2)		
O12—C3	1.43 (2)	C3—C4	1.44 (2)
C4—O13	1.44 (2)	O13—C5	1.40 (2)
C5—C6	1.44 (2)	C6—O14	1.35 (2)
O14—C7	1.41 (2)	C7—C8	1.43 (3)
C8—O15	1.37 (2)	O15—C9	1.38 (2)
C9—C10	1.15 (3)	C10—O16	1.45 (3)
O16—C11	1.34 (2)	C11—C16	1.39 (2)
C16—O12	1.38 (2)		
O17—C17	1.44 (2)	C17—C18	1.44 (2)
C18—O18	1.41 (2)	O18—C19	1.42 (2)
C19—C20	1.42 (2)	C20—O19	1.43 (2)
O19—C21	1.42 (2)	C21—C22	1.45 (2)
C22—O20	1.40 (2)	O20—C23	1.43 (2)
C23—C24	1.49 (2)	C24—O21	1.44 (2)
O21—C25	1.39 (2)	C25—C30	1.36 (2)
C30—O17	1.39 (2)		
O9· · ·O18	2.70 (1)	O9· · ·O20	2.69 (1)
O10· · ·O13	2.70 (2)	O10· · ·O17	2.81 (1)
O11· · ·O12	2.86 (1)	O11· · ·O15	2.66 (2)
O18· · ·O9· · ·O20	110.2 (4)	O13· · ·O10· · ·O17	112.3 (5)
O12· · ·O11· · ·O15	105.1 (5)		
C16—O12—C3—C4	66 (2)	O12—C3—C4—O13	50 (2)
C3—C4—O13—C5	−127 (2)	C4—O13—C5—C6	168 (1)
O13—C5—C6—O14	−64 (2)	C5—C6—O14—C7	173 (2)
C6—O14—C7—C8	163 (2)	O14—C7—C8—O15	49 (3)
C7—C8—O15—C9	−132 (2)	C8—O15—C9—C10	112 (3)
O15—C9—C10—O16	10 (4)	C9—C10—O16—C11	−130 (2)
C10—O16—C11—C16	167 (1)	O16—C11—C16—O12	−4 (2)
C11—C16—O12—C3	−168 (1)		
C30—O17—C17—C18	−74 (2)	O17—C17—C18—O18	−65 (1)
C17—C18—O18—C19	166 (1)	C18—O18—C19—C20	−162 (1)
O18—C19—C20—O19	67 (1)	C19—C20—O19—C21	−174 (1)
C20—O19—C21—C22	166 (1)	O19—C21—C22—O20	−68 (1)
C21—C22—O20—C23	167 (1)	C22—O20—C23—C24	−76 (2)
O20—C23—C24—O21	−60 (2)	C23—C24—O21—C25	168 (1)
C24—O21—C25—C30	−165 (1)	O21—C25—C30—O17	−2 (2)
C25—C30—O17—C17	159 (1)		

Lorentz–polarization corrections were applied. The structure was solved by the heavy-atom method and refined by full-matrix least squares on *F* with anisotropic displacement parameters for U, S and F atoms. H atoms were introduced in calculated positions and constrained to ride on their parent atom (C—H 0.95 Å, *B* 6 Å^2). All calculations were performed on a VAX 4200 computer.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Structure solution: *MolEN*. Structure refinement: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Preparation of material for publication: *MolEN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1160). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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