

**Data collection**

Siemens R3m diffractometer	$R_{\text{int}} = 0.0487$
$\omega$ - $2\theta$ 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 ( $\text{\AA}^2$ )

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

	$x$	$y$	$z$	$U_{\text{eq}}$
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 ( $\text{\AA}$ ,  $^\circ$ )

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 <sup>i</sup>	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 <sup>i</sup>	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 <sup>i</sup> —F4—Zr1	114.80 (13)
F2—Zr1—F4	86.3 (2)	C11—O11—Zr1	126.4 (3)
F4 <sup>i</sup> —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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**Pentaaquadioxouranium(VI) Triflate–18-Crown-6**

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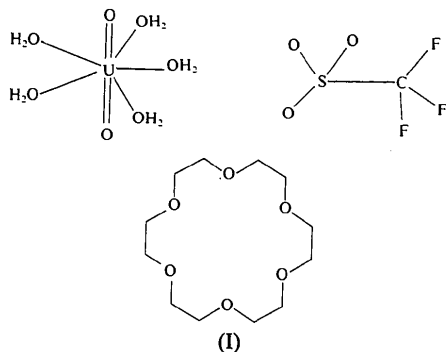
**Abstract**

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  $\text{CF}_3\text{SO}_3^-$  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  $\text{UO}_2$ -crown ether (Deshayes, Keller, Lance, Navaza, Nierlich & Vigner, 1994) and  $\text{UO}_2$ -azacrown (Nierlich, Sabattie, Keller, Lance & Vigner, 1994) inclusion compounds obtained in organic solution.

In order to investigate the effect of the solvent on the direct uranyl-crown coordination, the complexes obtained from aqueous solution were studied; we report here the structure of the title compound, (I).



The linear UO<sub>2</sub><sup>2+</sup> ion is coordinated to five O atoms from water molecules located in a plane perpendicular to the uranyl axis; the maximum deviations from the least-squares plane are ±0.05 (1) Å. The mean values of the U—O(uranyl) and U—O(water) bond distances [1.758 (2) and 2.41 (1) Å, respectively] are similar to those found in other compounds (Eller & Penneman, 1976; Deshayes, Keller, Lance, Nierlich & Vigner, 1993). There are two independent half crown ether molecules present, which have an imposed inversion centre. The C—C and C—O bond distances average 1.43 (11) and 1.41 (6) Å, respectively, and agree with those found in similar compounds (Deshayes, Keller, Lance, Navaza, Nierlich & Vigner, 1994). Torsion angles are given in Table 3: the macrocycles adopt two distorted conformations, *g*<sup>+</sup>*g*<sup>+</sup>*g*<sup>+</sup>*g*<sup>-</sup>*g*<sup>-</sup>*g*<sup>-</sup> and *g*<sup>-</sup>*g*<sup>+</sup>*g*<sup>-</sup>*g*<sup>+</sup>*g*<sup>+</sup>, different from those found in the inclusion compounds (Deshayes, Keller, Lance, Navaza, Nierlich & Vigner, 1994; Nierlich, Sabattie, Keller, Lance & Vigner, 1994).

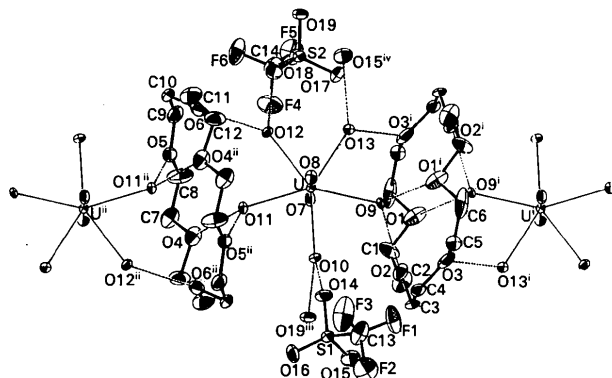


Fig. 1. ORTEP (Johnson, 1976) drawing of [(UO<sub>2</sub>)(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub><sup>-</sup>·(18-crown-6) showing the atom-labelling scheme. Displacement ellipsoids are shown at the 30% probability level.

The H atoms were not observed, but there are short intermolecular contacts between O(water) and O(triflate) and O(crown ether) [ranging from 2.67 (2) to 2.81 (1) Å]. This suggests that hydrogen bonding occurs between H<sub>2</sub>O and the triflate and crown ether moieties. Each crown ether is shared by two UO<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub> units to form polymeric chains as shown in Fig. 1.

## Experimental

Crystals of the title compound were obtained by evaporation of an aqueous solution of crown ether and uranyl trifluoromethanesulfonate.

### Crystal data

[UO<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>](CF<sub>3</sub>SO<sub>3</sub>S)<sub>2</sub>·  
C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>  
*M<sub>r</sub>* = 922.56  
Triclinic  
*P* $\bar{1}$   
*a* = 10.411 (7) Å  
*b* = 10.760 (5) Å  
*c* = 15.801 (8) Å  
 $\alpha$  = 83.52 (4)°  
 $\beta$  = 89.78 (5)°  
 $\gamma$  = 61.41 (5)°  
*V* = 1542 (3) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.987 Mg m<sup>-3</sup>

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
Cell parameters from 25 reflections  
 $\theta$  = 8–12°  
 $\mu$  = 5.23 mm<sup>-1</sup>  
*T* = 295 K  
Irregular  
0.40 × 0.30 × 0.20 mm  
Yellow

### Data collection

CAD-4 diffractometer  
 $\omega/2\theta$  scans  
Absorption correction:  
empirical (DIFABS;  
Walker & Stuart, 1983)  
*T<sub>min</sub>* = 0.926, *T<sub>max</sub>* =  
1.066  
4752 measured reflections  
4272 independent reflections  
3459 observed reflections  
 $|I| > 3\sigma(I)$

*R<sub>int</sub>* = 0.021  
 $\theta_{\text{max}}$  = 23°  
*h* = 0 → 11  
*k* = -11 → 11  
*l* = -17 → 17  
3 standard reflections  
frequency: 60 min  
intensity variation:  
-3.8% in 65 h

### Refinement

Refinement on *F*  
*R* = 0.045  
*wR* = 0.061  
*S* = 2.5  
3459 reflections  
379 parameters  
H atoms not located  
*w* = 1/ $\sigma^2(F)$

( $\Delta/\sigma$ )<sub>max</sub> = 0.11  
 $\Delta\rho_{\text{max}}$  = 0.95 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -0.25 e Å<sup>-3</sup>  
Atomic scattering factors  
from *International Tables*  
for X-ray Crystallography  
(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i>
U	0.02884 (4)	0.00799 (4)	0.24744 (3)	2.725 (9)
S(1)	-0.6198 (4)	0.2501 (4)	0.2319 (2)	4.67 (9)
S(2)	0.6268 (3)	-0.2404 (4)	0.2747 (2)	4.56 (8)

F(1)	-0.675 (2)	0.423 (1)	0.3465 (7)	11.6 (5)	C(1)—C(2)	1.43 (3)	C(3)—C(4)	1.51 (3)
F(2)	-0.861 (1)	0.457 (2)	0.273 (1)	14.9 (6)	C(5)—C(6)	1.22 (3)	C(7)—C(8)	1.40 (3)
F(3)	-0.722 (2)	0.521 (1)	0.221 (1)	17.6 (8)	C(9)—C(10)	1.48 (3)	C(11)—C(12)	1.52 (3)
F(4)	0.618 (1)	-0.470 (1)	0.249 (1)	13.3 (4)	C(1)—O(1)—C(6 <sup>i</sup> )	117 (2)	C(2)—O(2)—C(3)	113 (1)
F(5)	0.817 (2)	-0.511 (1)	0.3076 (9)	12.3 (5)	C(4)—O(3)—C(5)	115 (2)	C(7)—O(4)—C(12 <sup>ii</sup> )	111 (2)
F(6)	0.764 (2)	-0.431 (1)	0.1730 (8)	12.8 (5)	C(8)—O(5)—C(9)	111 (1)	C(10)—O(6)—C(11)	111 (1)
O(1)	0.127 (1)	-0.284 (1)	0.526 (1)	10.8 (4)	O(1)—C(1)—C(2)	112 (2)	O(2)—C(2)—C(1)	115 (2)
O(2)	-0.171 (1)	-0.115 (1)	0.4603 (7)	8.0 (3)	O(2)—C(3)—C(4)	111 (1)	O(3)—C(4)—C(3)	105 (1)
O(3)	-0.303 (1)	0.149 (1)	0.5149 (7)	7.6 (3)	O(3)—C(5)—C(6)	124 (2)	O(1)—C(6 <sup>i</sup> )—C(5 <sup>i</sup> )	124 (2)
O(4)	0.044 (1)	-0.265 (1)	0.0357 (8)	7.8 (4)	O(4)—C(7)—C(8)	115 (2)	O(5)—C(8)—C(7)	112 (2)
O(5)	0.2737 (9)	-0.202 (1)	-0.0215 (7)	6.7 (3)	O(5)—C(9)—C(10)	109 (1)	O(6)—C(10)—C(9)	110 (1)
O(6)	0.255 (1)	0.063 (1)	-0.0036 (7)	8.3 (4)	O(6)—C(11)—C(12)	111 (1)	O(4)—C(12 <sup>ii</sup> )—C(11 <sup>ii</sup> )	116 (2)
O(7)	0.116 (1)	-0.1769 (9)	0.2794 (6)	4.6 (2)	<b>Hydrogen-bond geometry</b>			
O(8)	-0.061 (1)	0.1935 (8)	0.2162 (6)	5.0 (3)	O(9)···O(1 <sup>i</sup> )	2.81 (1)	O(9)···O(2)	2.717 (9)
O(9)	-0.0448 (8)	0.0409 (8)	0.3918 (5)	3.8 (2)	O(10)···O(14)	2.68 (1)	O(10)···O(19 <sup>iii</sup> )	2.71 (1)
O(10)	-0.2027 (8)	0.0136 (9)	0.2524 (6)	4.5 (2)	O(11)···O(4)	2.78 (1)	O(11)···O(5 <sup>ii</sup> )	2.73 (2)
O(11)	-0.0221 (8)	-0.0150 (9)	0.1032 (5)	4.1 (2)	O(12)···O(6)	2.73 (2)	O(12)···O(18)	2.67 (2)
O(12)	0.2339 (8)	-0.025 (1)	0.1621 (5)	4.8 (2)	O(13)···O(3 <sup>i</sup> )	2.70 (1)	O(13)···O(15 <sup>iv</sup> )	2.69 (2)
O(13)	0.2163 (8)	0.0163 (9)	0.3325 (5)	4.5 (2)	O(1 <sup>i</sup> )···O(9)···O(2)	111.1 (3)	O(14)···O(10)···O(19 <sup>iii</sup> )	101.8 (3)
O(14)	-0.4750 (9)	0.234 (1)	0.2297 (8)	6.6 (3)	O(4)···O(11)···O(5 <sup>ii</sup> )	108.7 (5)	O(6)···O(12)···O(18)	95.6 (6)
O(15)	-0.628 (1)	0.155 (1)	0.2992 (8)	8.4 (4)	O(3 <sup>i</sup> )···O(13)···O(15 <sup>iv</sup> )	111.5 (8)		
O(16)	-0.685 (1)	0.266 (1)	0.1521 (7)	8.2 (4)	<b>Symmetry codes: (i) -x, -y, 1 - z; (ii) -x, -y, -z; (iii) x - 1, y, z; (iv) 1 + x, y, z.</b>			
O(17)	0.573 (1)	-0.247 (1)	0.3573 (7)	7.8 (3)				
O(18)	0.522 (1)	-0.160 (1)	0.2024 (7)	7.1 (3)				
O(19)	0.7455 (9)	-0.212 (1)	0.2738 (7)	5.9 (3)				
C(1)	0.044 (2)	-0.335 (2)	0.480 (2)	10.2 (5)				
C(2)	-0.109 (3)	-0.255 (2)	0.490 (2)	13.7 (8)				
C(3)	-0.323 (1)	-0.041 (2)	0.472 (1)	5.9 (4)				
C(4)	-0.382 (1)	0.118 (2)	0.455 (1)	7.6 (5)				
C(5)	-0.344 (2)	0.301 (2)	0.512 (2)	10.7 (7)				
C(6)	-0.274 (2)	0.354 (2)	0.477 (2)	13 (1)				
C(7)	0.171 (2)	-0.359 (2)	0.006 (1)	9.6 (7)				
C(8)	0.291 (2)	-0.339 (2)	0.024 (2)	8.6 (6)				
C(9)	0.402 (2)	-0.192 (2)	-0.010 (1)	8.5 (7)				
C(10)	0.375 (2)	-0.049 (2)	-0.047 (1)	6.2 (4)				
C(11)	0.216 (2)	0.192 (2)	-0.043 (2)	12.6 (7)				
C(12)	0.063 (2)	0.297 (2)	-0.020 (2)	12.0 (7)				
C(13)	-0.716 (3)	0.425 (2)	0.272 (1)	10.9 (8)				
C(14)	0.712 (2)	-0.424 (2)	0.249 (1)	11.1 (7)				

Table 2. Selected geometric parameters (Å, °)

<b>U environment</b>			
U—O(7)	1.756 (5)	U—O(8)	1.760 (5)
U—O(9)	2.414 (3)	U—O(10)	2.384 (3)
U—O(11)	2.41 (1)	U—O(12)	2.42 (2)
U—O(13)	2.42 (2)		
O(7)—U—O(8)	179.0 (1)		
<b>Triflate</b>			
S(1)—O(14)	1.43 (2)	S(2)—O(17)	1.43 (2)
S(1)—O(15)	1.43 (2)	S(2)—O(18)	1.46 (2)
S(1)—O(16)	1.39 (2)	S(2)—O(19)	1.41 (2)
S(1)—C(13)	1.85 (3)	S(2)—C(14)	1.84 (2)
C(13)—F(1)	1.25 (3)	C(14)—F(4)	1.29 (2)
C(13)—F(2)	1.38 (2)	C(14)—F(5)	1.32 (2)
C(13)—F(3)	1.22 (3)	C(14)—F(6)	1.31 (2)
O(14)—S(1)—O(15)	111 (1)	O(17)—S(2)—O(18)	119 (1)
O(14)—S(1)—O(16)	114 (1)	O(17)—S(2)—O(19)	114 (1)
O(14)—S(1)—C(13)	99 (1)	O(17)—S(2)—C(14)	105 (1)
O(15)—S(1)—O(16)	119 (1)	O(18)—S(2)—O(19)	112 (1)
O(15)—S(1)—C(13)	103 (1)	O(18)—S(2)—C(14)	103 (1)
O(16)—S(1)—C(13)	107 (1)	O(19)—S(2)—C(14)	103 (1)
S(1)—C(13)—F(1)	113 (2)	S(2)—C(14)—F(4)	111 (1)
S(1)—C(13)—F(2)	105 (2)	S(2)—C(14)—F(5)	110 (1)
S(1)—C(13)—F(3)	112 (2)	S(2)—C(14)—F(6)	110 (1)
F(1)—C(13)—F(2)	107 (2)	F(4)—C(14)—F(5)	107 (1)
F(1)—C(13)—F(3)	116 (2)	F(4)—C(14)—F(6)	108 (1)
F(2)—C(13)—F(3)	102 (1)	F(5)—C(14)—F(6)	111 (1)
<b>18-Crown-6</b>			
O(1)—C(1)	1.45 (2)	O(1)—C(6 <sup>i</sup> )	1.35 (3)
O(2)—C(2)	1.35 (2)	O(2)—C(3)	1.42 (2)
O(3)—C(4)	1.42 (2)	O(3)—C(5)	1.47 (2)
O(4)—C(7)	1.35 (2)	O(4)—C(12 <sup>ii</sup> )	1.34 (2)
O(5)—C(8)	1.50 (2)	O(5)—C(9)	1.41 (2)
O(6)—C(10)	1.49 (2)	O(6)—C(11)	1.32 (2)

Table 3. Torsion angles (°) for 18-crown-6

O(1)—C(1)—C(2)—O(2)	60 (2)
O(2)—C(3)—C(4)—O(3)	-60 (2)
O(3)—C(5)—C(6)—O(1 <sup>i</sup> )	-33 (3)
C(6 <sup>i</sup> )—O(1)—C(1)—C(2)	179 (2)
C(1)—O(1)—C(6 <sup>i</sup> )—C(5 <sup>i</sup> )	115 (3)
C(3)—O(2)—C(2)—C(1)	-179 (2)
C(2)—O(2)—C(3)—C(4)	169 (2)
C(5)—O(3)—C(4)—C(3)	-179 (2)
C(4)—O(3)—C(5)—C(6)	-101 (2)
O(4)—C(7)—C(8)—O(5)	-66 (2)
O(5)—C(9)—C(10)—O(6)	61 (2)
O(6)—C(11)—C(12)—O(4 <sup>ii</sup> )	-56 (2)
C(12 <sup>ii</sup> )—O(4)—C(7)—C(8)	-176 (2)
C(7)—O(4)—C(12 <sup>ii</sup> )—C(11 <sup>ii</sup> )	-174 (2)
C(9)—O(5)—C(8)—C(7)	-174 (2)
C(8)—O(5)—C(9)—C(10)	-174 (2)
C(11)—O(6)—C(10)—C(9)	-172 (2)
C(10)—O(6)—C(11)—C(12)	-159 (1)

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

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Programs used: *MolEN* (Fair, 1990), *ORTEP* (Johnson, 1976), *DI-FABS* (Walker & Stuart, 1983). The structure was solved by the heavy-atom method and refined using a full-matrix least-squares method with anisotropic displacement parameters. All calculations were performed on a VAX 4200 computer.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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**[(5a,6,7,8,9,9a- $\eta^6$ )-[1,4]Benzodioxino[2,3-*b*]pyridine)( $\eta^5$ -cyclopentadienyl)iron(II) Hexafluorophosphate**

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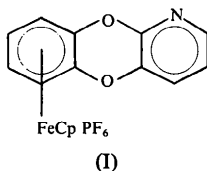
(Received 3 September 1993; accepted 25 March 1994)

**Abstract**

The structure of [(5a,6,7,8,9,9a- $\eta^6$ )-[1,4]benzodioxino[2,3-*b*]pyridine)( $\eta^5$ -cyclopentadienyl)iron(II) hexafluorophosphate, [Fe(C<sub>5</sub>H<sub>5</sub>)(C<sub>11</sub>H<sub>7</sub>NO<sub>2</sub>)]PF<sub>6</sub>, has been studied. The dihedral angle between the benzene and pyridine rings of the ligand system is 177.4 (3)°; the benzene and cyclopentadienyl rings are nearly parallel [dihedral angle 1.3 (4)°]. The Fe atom is closer to the benzene ring [1.542 (4) Å] than to the cyclopentadienyl (Cp) ring [1.652 (5) Å] and it is located within the fold of the heterocyclic ligand.

**Comment**

The title complex (I) was synthesized following the procedure of Sutherland, Piórko, Lee, Simonsen & Lynch (1988) by the reaction of 2,3-dihydropyridine with ( $\eta^6$ -1,2-dichlorobenzene)( $\eta^5$ -Cp)iron(II) hexafluorophosphate. Results obtained in the course of this work supplement earlier studies of the structure of tricyclic heterocycles complexed with the FeCp moiety.



In (I), the Fe atom is centred above the Cp ring while the longest Fe—C(arene) distances are found for the atoms C5a [2.116 (8) Å], C9 [2.097 (7) Å] and

C9a [2.096 (7) Å]. The central dioxin ring is symmetrical, unlike that in the FeCp complex of 2-methylidibenzodioxin (Abboud, Simonsen, Piórko & Sutherland, 1991). The distances between the Fe atom and the Cp ring plane [1.652 (5) Å] and between Fe and the coordinated arene ring plane [1.542 (4) Å] are within the range reported for FeCp complexes of arenes (Houlton, Roberts, Silver, Wells & Frampton, 1992). The planes of the coordinated benzene ring and Cp ring are nearly parallel [1.3 (4)°] and the FeCp moiety is located within the fold of the heterocyclic ligand; both these results have been reported for similar complexes (Abboud, Simonsen, Piórko & Sutherland, 1991; Abboud, Lynch, Simonsen, Piórko & Sutherland, 1990; Sutherland, Piórko, Lee, Simonsen & Lynch, 1988; Lynch, Thomas, Simonsen, Piórko & Sutherland, 1986; Simonsen, Lynch, Sutherland & Piórko, 1985). The dihedral angle between the benzene and pyridine rings of the ligand system is 177.4 (3)°, which is smaller than the angle found in 2,7,8-trinitro-1,4-benzodioxino[2,3-*b*]pyridine [174.65 (8)°; Piórko, Christie, Crook & Sampson, 1994]. (The structure of 1,4-benzodioxino[2,3-*b*]pyridine has not been reported.)

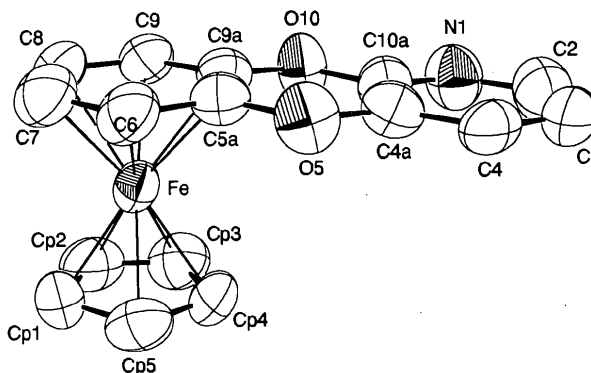


Fig. 1. Molecular structure of the cation of (I) with atom numbering. Displacement ellipsoids are at the 50% probability level.

**Experimental**

The complex was synthesized according to the method described by Sutherland, Piórko, Lee, Simonsen & Lynch (1988). The crystal used for data collection was grown from acetone-diethyl ether-dichloromethane solution at ca 255 K.

*Crystal data*

[Fe(C<sub>5</sub>H<sub>5</sub>)(C<sub>11</sub>H<sub>7</sub>NO<sub>2</sub>)]PF<sub>6</sub>

*M<sub>r</sub>* = 451.08

Monoclinic

*P*2<sub>1</sub>/*n*

*a* = 8.053 (3) Å

*b* = 13.955 (2) Å

*c* = 14.843 (6) Å

$\beta$  = 97.12 (2)°

Mo *K* $\alpha$  radiation

$\lambda$  = 0.7107 Å

Cell parameters from 24

reflections

$\theta$  = 28–38°

$\mu$  = 1.08 mm<sup>-1</sup>

*T* = 290 K

Parallelepiped